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PROCEEDINGS

OF THE

PHYSICAL SOCIETY OF LONDON.

From December 1915 *to August* 1916.

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PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1915–1916.

October 22, 1915.

Meeting held at Imperial College of Science.

Dr. A. Russell, M.A., Vice-President, in the Chair.

The following Papers were read :—

1. "The Radiation and Convection from a Heated Wire in an Enclosure of Air." By T. Barratt, A.R C.Sc., D.Sc.

2. "On the Determination, by the Method of Diffusive Convection, of the Coefficient of Diffusion of a Salt Dissolved in Water." By A. Griffiths, D.Sc.

3.* "The Magnitude of the Thermal Resistance Introduced at the Slightly Conical Junction of Two Solids and Its Variation with the Nature of the Surfaces in Contact." By T. Barratt, A.R.C.S., D.Sc.

* Taken as read.

November 12, 1915.

Meeting held at Imperial College of Science.

Dr. A. **Russell**, M.A., Vice-President, in the Chair.

The following Paper was read :—

"The Effect of Electric Oscillations on the Magnetic Properties of Iron, Investigated by the Campograph." By Prof. J. A. **Fleming**, M.A., D.Sc., F.R.S., and P. R. **Coursey**, B.Sc.

The following Demonstrations were given by Mr. R. S. **Whipple**:

1. A Hydraulic Analogy of a Wheatstone Bridge.
2. A Lecture Table Method of Obtaining Recalescence Curves.
3. The Leeds and Northrup Recorder.

November 26, 1915.

Meeting held at Imperial College of Science.

Dr. A. **Russell**, M.A., Vice-President, in the Chair.

The following Papers were read :—

1. "On Obtaining and Maintaining a Bright Hydrogen Spectrum, with Special Reference to the 4,341 Line." By J. **Guild**, A.R.C.S., D.I.C., F.R.A.S.

2. "Determination of the Coefficient of Diffusion of Potassium Chloride by an Analytical Method." By A. **Griffiths**, D.Sc.

3. "Exhibition of Apparatus for Evaluating Elliptic Integrals." By A. F. **Ravenshear**.

January 28, 1916.

Meeting held at Imperial College of Science.

Prof. Sir J. J. **Thomson**, O.M., F.R.S., President, in the Chair.

The Second Guthrie Lecture was delivered by Mr. W. B. **Hardy**, M.A., Sec. R.S., on

"Some Properties of Living Matter."

Annual General Meeting.

February 11, 1916.

Meeting held at the Imperial College of Science.

Dr. A. RUSSELL, M.A., Vice-President, in the Chair.

The Report of the Council was read by the Secretary.

In the year 1915 thirteen ordinary meetings have been held. The average attendance at the meetings was 37.

In response to the invitation circulated in July several Fellows sent suggestions to the President with respect to inventions which might be used or developed in connection with the war. The War Register forms which were circulated at the same time were returned duly completed by 185 Fellows. A classified list of these returns was made by the Admiralty Board of Invention and Research. The London County Council Education Office, acting on behalf of the Metropolitan Munitions Committee, made a classified list of the Fellows residing within the Metropolitan area who offered their services.

A complete classified Register of the returns has been made by a Committee of the Council with the co-operation of Mr. R. J. Sowter, a Fellow of the Society.

Copies of this Register are in the hands of the various Government Departments and the Council has reason to believe that they have been found useful.

The Second Guthrie Lecture, which was to have been delivered in October, had to be postponed owing to the illness of the lecturer (Mr. W. B. Hardy, F.R.S.).

The Annual Exhibition of Apparatus was again suspended owing to the war.

The number of Ordinary Fellows on the Roll on December 31, 1915, as distinct from Honorary Fellows, was 438. Eight new Fellows have been elected, and there have been seven resignations.

The Society has to mourn the loss of twelve Ordinary Fellows—namely, Prof. W. G. Adams and Sir Arthur Rücker (Past Presidents of the Society), Prof. F. R. Barrell, Dr. H. Debus, Capt. H. J. Dockrell, Prof. R. Meldola, Mr. H. G. J. Moseley (killed in action), Mr. F. H. Neville, Sir Andrew Noble, Sir Henry Roscoe, Prof. J. Shand and Mr. H. A. Taylor.

The Report was adopted by the meeting.

The Report of the Treasurer and the Balance-sheet were presented by the Treasurer.

The total income of the Society shows a decrease this year of about £54 when compared with last year. The most serious decrease is in the subscriptions. The annual subscriptions are £45 down, and there have been no Life Compositions during the year. The increase in the sales of publications is very satisfactory, and the gain under this head has practically wiped out the drop in the subscriptions.

The expenditure for the year has decreased by about £40. The decrease would have been greater if it had not been for the considerable increase (£71) in the cost of the "Proceedings," owing to the large number of pages that have been published during the year. It is also to be noted that last year there was additional expenditure due to a lecture and report.

The Society's income has exceeded its expenditure by £88. 4s. 5d., which shows that the Society, in spite of the present War conditions, is still sound financially.

The total assets show a decrease of about £90; this is caused by the depreciation in the value of the securities, based on the values on January 1st, 1916, which were kindly supplied by Messrs. Parr's Bank, Limited.

Arrears in the subscriptions have increased. The amount given in the Accounts is what is actually due to the Society, but I do not anticipate, under existing conditions, that we shall recover more than one-half the amount.

The liabilities on account of the Life Composition Fund are lower by £91. 10s., owing to the decease of seven Life Fellows.

The balance available in the General Fund is practically stationary.

The Report of the Treasurer was adopted.

The Treasurer in Account with the Physical Society, from January, 1915, to December 31st, 1915.

Dr.	£	s.	d.	£	s.	d.
Entrance Fees	7	7	0			
Subscriptions	495	13	3			
Extra Subscriptions	17	17	0			
Arrears	14	14	0			
Subscriptions paid in Advance	2	2	0			
Students' Subscriptions	3	13	6			
Subscriptions for "Science Abstracts" and Advance Proofs	13	14	6			
				555	1	3
Composition Fees				Nil.		
Dividends :—						
Furness Debenture Stock	14	8	6			
Midland Railway	35	16	8			
Metropolitan Board of Works	6	4	2			
Lancaster Corporation Stock	10	13	0			
New South Wales	7	17	6			
London, Brighton & South Coast Railway	21	10	10			
Great Eastern Railway	18	0	10			
India 3½% Stock	15	10	0			
				130	1	6
Interest on deposit account				9	9	5
Sales of Publications ("The Electrician" Printing & Publishing Co.)				163	2	0
				857	14	2
Transferred from Deposit Account				100	0	0
Balance at Bank, January 1, 1915	32	8	5			
Less Two Cheques	4	19	5			
				27	9	0
				£985	3	2

Cr.	£	s.	d.	£	s.	d.
"Science Abstracts"				281	16	6
Printing and Distributing Publications of the Society :—						
"The Electrician" Printing & Publishing Co.—						
"Proceedings"	301	13	7			
Bulletin	24	14	6			
Distribution	52	13	11			
General	37	4	1			
	416	6	1			
Less credit for use of type	2	2	8			
				414	3	5
Periodicals	1	15	0			
Reporting	35	0	0			
Refreshments and Attendance	9	12	3			
Petty cash	15	16	1			
Bank commission			10			
Royal Asiatic Society	2	2	0			
International Catalogue	5	16	2			
Hodgson, Mathematical Notation	1	5	6			
War Register	2	2	0			
				73	9	10
				769	9	9
To Deposit Account, April				100	0	0
Balance at Bank, January 1, 1916				115	13	5
				£985	3	2

WILLIAM DUDDELL, *Honorary Treasurer.*

Audited and found correct,

J. E. KINGSBURY.
J. W. CAPSTICK.

January 21st, 1916.

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, December 31st, 1915.

Assets.	£	s.	d.
Subscriptions due, Treasurer's estimate...	40	8	6
£533 Furness Railway 3 per cent. Debenture Stock	370	0	0
£1,600 Midland Railway 2½ per cent. Preference Stock	924	0	0
£200 Metropolitan Board of Works 3½ per cent. Consolidated Stock	190	0	0
£400 Lancaster Corporation 3 per cent. Redeemable Stock	306	0	0
£254. 2s. 9d. New South Wales 3½ per cent. Debenture Stock	230	0	0
£500 London, Brighton & South Coast Railway Ordinary Stock	368	0	0
£500 Great Eastern Railway 4 per cent. Debenture Inscribed Stock........	475	0	0
£500 India 3½ per cent Stock	404	0	0
Balance at Bank	115	13	5
Ditto on deposit........	300	0	0
Publications (Treasurer's Estimate)........	220	0	0
	£3,943	1	11

Liabilities.	£	s.	d
Life Compositions	2,010	10	0
Balance General Fund........	1,932	11	11
	£3,943	1	11

WILLIAM DUDDELL, *Honorary Treasurer.*

Audited and found correct,

J. E. KINGSBURY.
J. W. CAPSTICK.

January 21st, 1916.

LIFE COMPOSITION FUND.

	£	s.	d.
164 Fellows paid £10	1,640	0	0
3 Fellows paid £15	45	0	0
5 Fellows paid £21	105	0	0
7 Fellows paid £31. 10s.	220	10	0
	£2,010	10	0

NOTE.—Two Fellows who paid £10 deceased during year 1914 (not deducted in last account).

Four Fellows who paid £10 deceased during year 1915.

One Fellow who paid £31 10s., deceased during year 1915.

Audited and found correct,

WILLIAM DUDDELL, *Honorary Treasurer.*
January 21st, 1916.

J. E. KINGSBURY.
J. W. CAPSTICK.

The Election of Officers and Council then took place, the new Council being constituted as follows :—

President.—Prof. C. VERNON BOYS, F.R.S.

Vice-Presidents, who have filled the Office of President.—Prof. G. C. FOSTER, D.Sc., LL.D., F.R.S. ; Prof. R. B. CLIFTON, M.A., F.R.S. ; Prof. A. W. REINOLD, C.B., M.A., F.R.S. ; Sir W. DE W. ABNEY, R.E., K.C.B., D.C.L., F.R.S. ; Prin. Sir OLIVER J. LODGE, D.Sc., LL.D., F.R.S. ; Prof. SILVANUS P. THOMPSON, D.Sc., F.R.S. ; R. T. GLAZEBROOK, C.B., D.Sc., F.R.S. ; Prof. J. PERRY, D.Sc., F.R.S. ; C. CHREE, Sc.D., LL.D., F.R.S. ; Prof. H. L. CALLENDAR, M.A., LL.D., F.R.S. ; Prof. A. SCHUSTER, Ph.D., Sc.D., F.R.S. ; Sir J. J. THOMSON, O.M., D.Sc., F.R.S.

Vice-Presidents.—W. R. COOPER, M.A., B.Sc. ; F. E. SMITH ; S. W. J. SMITH, M.A., D.Sc., F.R.S. ; W. E. SUMPNER, D.Sc.

Secretaries.—W. ECCLES, D.Sc. ; R. S. WILLOWS, M.A., D.Sc.

Foreign Secretary.—R. T. GLAZEBROOK, C.B., D.Sc., F.R.S.

Treasurer.—W. DUDDELL, F.R.S.

Librarian.—S. W. J. SMITH, M.A., D.Sc., F.R.S.

Other Members of Council.—H. S. ALLEN, M.A., D.Sc. ; Prof. W. H. BRAGG, M.A., F.R.S. ; S. D. CHALMERS, M.A. ; Prof. G. W. O. HOWE, D.Sc. ; Prof. J. W. NICHOLSON, M.A., D.Sc. ; C. C. PATERSON ; C. E. S. PHILLIPS, F.R.S.E. ; Prof. O. W. RICHARDSON, M.A., D.Sc., F.R.S. ; G. F. C. SEARLE, Sc.D., F.R.S. ; F. J. W. WHIPPLE, M.A.

After the conclusion of the General Business, the Chair was taken by Prof. C. V. BOYS and the following Papers were read :—

1. "On a General Bridge Method for Comparing the Mutual Inductance between Two Coils with the Self Inductance of One of Them." By Prof. C. H. LEES, F.R.S.

2. "An Enclosed Cadmium Vapour Arc Lamp." By H. J. S. SAND, D.Sc.

Two Slides were shown by Dr. SYDNEY RUSS showing the Ultra-violet Spectrum of the Simpson Arc, compared with that of Tungsten.

March 10, 1916.

Meeting held at Imperial College of Science.

Prof. C. V. Boys, F.R.S., President, in the Chair.

The following Papers were read :—

1. "Experiments Illustrating the Flow of Heat in Conducting Sheets." By S. Skinner, M.A.
2. "The Absorption of Gases by Quartz Vacuum Tubes." By R. S. Willows, M.A., D.Sc., and H. Trevelyan George, M.A.

March 24, 1916.

Meeting held at the Imperial College of Science.

Mr. F. E. Smith, A.R.C.S., Vice-President, in the Chair.

The following Papers were read :—

1. "A New Method of Determining Ionic Velocities." By Mrs. C. H. Griffiths, B.Sc.
2. "Note on an Explanation of the Migration of the Ions." By S. W. J. Smith, D.Sc., F.R.S.
3.* "A Method of Exhibiting the Velocity of Iodine Ions in Solution." By S. W. J. Smith, D.Sc. F.R.S.

* Taken as read.

May 12, 1916.

Meeting held at Imperial College of Science.

Prof. C. V. Boys, F.R.S., President, in the Chair.

The following Papers were read :—

1. "The Latent Heat of Fusion of Metals and the Quantum-Theory." By Dr. H. S. Allen, M.A.
2. "Lenses for Light Distribution." By T. Smith, B.A.
3. "The Choice of Glass for Cemented Objectives." By T. Smith, B.A.

May 26, 1916.

Meeting held at Imperial College of Science.

Prof. C. V. **Boys**, F.R.S., President, in the Chair.

The following Papers were read :—

1. "The Correction of Chromatic Aberrations when the External Media are Dispersive." By T. **Smith**, B.A.

2. "Note on the Use of the Auto-Collimating Telescope in the Measurement of Angles." By J. **Guild**, F.R.A.S.

3. "The Viscosity of Colloidal Solutions." By E. **Hatschek**.

June 16, 1916.

Meeting held at Imperial College of Science.

Prof. G. W. O. **Howe**, D.Sc., in the Chair.

The following Papers were read :—

1. "Experiments with Mercury Jet Interruptors." By Capt. C. E. S. **Phillips**, F.R.S.E.

2. "A Method of Measuring the Pressure of Light by Means of Thin Metal Foil." Part II. By G. D. **West**, B.Sc.

3. "The Viscosity of Suspensions of Rigid Particles at Different Rates of Shear." By **Edith Humphrey**, B.Sc., Ph.D., and **Emil Hatschek**.

4.* "A Correction of Some Work on Diffusion by Dr. A. Griffiths and Others." By A. **Griffiths**, D.Sc.

* Taken as read.

June 30, 1916.

Meeting held at Imperial College of Science.

Prof. C. V. **Boys**, F.R.S., President, in the Chair.

The following Papers were read :—

1. "A Sensitive Magnetometer." By P. E. **Shaw**, D.Sc., and C. **Hayes**, B.Sc.

2. "The Latent Heat of Fusion of a Metal and the Quantum-Theory." By H. S. **Allen**, D.Sc.

3.* "Cohesion." Part II. By Prof. H. **Chatley**.

Some Experiments on the Thermo-electric Properties of Fused Metals were shown by **Chas. R. Darling**, A.R.C.S.

* Taken as read.

I. *The Radiation and Convection from a Heated Wire in an Enclosure of Air.* *By* Thomas Barratt, *A.R.C.S., D.Sc.*

Received June 22, 1915.

1. *Objects of Experiment.*

When the temperature of a metallic wire or cylindrical rod placed in the open air or in an enclosure at constant temperature containing a gas is raised above that of the gas, it is found that the loss of heat H from the wire is very nearly proportional to its excess of temperature V above that of the gas surrounding it. Assuming that the loss of heat is entirely due to convection, Boussinesq[*] has obtained this result mathematically in the case of the convection of heat by a stream of liquid from a cylinder maintained at constant temperature. Experimental results by Compan[†] (in the case of spheres heated in air) and Kennelly[‡] and others (for metallic wires heated in air by an electric current) have verified this conclusion. The truth of Newton's law ($H \propto V$) has also been assumed, with justifiable results, in its application to various instruments of precision, such as hot-wire ammeters, and, quite recently, anemometers.[§] In an arrangement of apparatus adopted by the present author[||] for the measurement of thermal conductivity (*see* fiigure on next page), the law was found to be accurately true up to an excess of temperature of, at any rate, 12°C.

It seems to be generally admitted that Newton's law is applicable, with great accuracy, to that portion of the heat which is lost by convection, even when the temperature of the heated body is raised many degrees above that of its surroundings, but that the radiation loss by no means conforms to that law. Assuming for the moment that Stefan's "fourth power" law applies to the part of the heat, R lost by radiation from a heated metallic wire, we have

$$R = \sigma(\theta^4 - \theta_0^4),$$

---

[*] Boussinesq, "Comp. Rend.," CXXXIII., p. 257, 1901. *See also* A. Russell, "Proc." Phys. Soc., XXII., p. 432, 1909; and L. V. King, Roy. Soc. "Phil. Trans.," 373, Nov. 12, 1914.

[†] P. Compan, "Ann. de Chim. et Phys.," XXVI., p. 488, 1902.

[‡] Kennelly and Sanborn, Amer. Phil. Soc. "Proc.," 55-77, 1914.

[§] J. T. Morris, "The Electrician," p. 1056, Oct. 4, 1912; "Engineering," Aug. 8, 1913.; L. V. King, *loc. cit.*

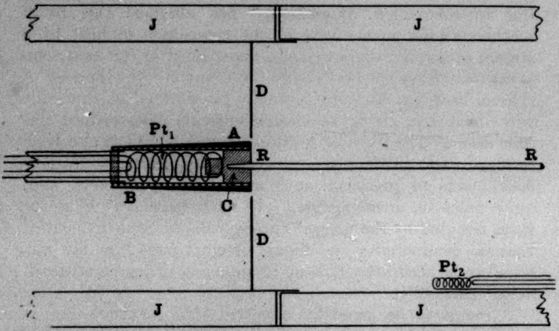
[||] T. Barratt, "Proc." Phys. Soc., XXVI., V., 346, Aug. 1914.

where σ is constant, and θ and θ_0 are the absolute temperatures of the hot body and its surroundings respectively. If we put $\theta=\theta_0+x$, we have

$$R=\sigma x4\theta_0^3\{1+3x/(2\theta_0)+x^2/\theta_0^2+x^3/(4\theta_0)^3\}.$$

Hence, R is proportional to x provided that $3x/(2\theta_0)$ can be neglected compared to unity. (For example, the heat lost for 2°C. excess at air temperature is twice that lost for 1°C. excess to within 1 part in 200.)

If then the radiation loss is only a small percentage of the convection, we should expect Newton's law for the convective heat loss to apply for the total heat loss for small differences of temperature.



RR=rod or wire; C=solid copper cylinder; AB=copper cylinder tapering in thickness from 2mms. to zero; Pt_1 and Pt_2=platinum thermometers; DD=thin copper disc dividing enclosure into two compartments; JJJJ=water or steam jacket.

As far as one can find from recent literature on the subject, no experimental work has been attempted with the direct object of determining the relation between the amounts of radiation and convection from a body heated in an enclosure of gas. Kennelly * was uncertain of the correction for radiation from a hot wire, but finally assumed that a copper wire radiates 94 per cent. as much heat as a black body at the same tempera-

---

* A. E. Kennelly, "Trans." Amer. Inst. Elec. Eng., XXVII., I., 363, 1909.

ture. This correction then amounted to about 2 per cent. for the smallest wire, and about 8 per cent. of the total energy for the largest wire employed.

Langmuir, however, referring to the above Paper, remarks : " Hence it would have been better for Kennelly to neglect the small percentage due to radiation from copper, as the radiation is probably less than 1 per cent." (Irving Langmuir, Amer. Inst. Elec. Eng., June 25, 1912.) In a previous Paper Langmuir (" Phys. Rev.," XXXIV., p. 401, 1912) asserts that: " Radiation from small metallic wires is practically negligible compared to convection up to several hundred degrees." L. V. King (*loc. cit.*) says : " In the present work the heat lost by radiation plays a very subordinate part, and was not made the subject of special investigation."

It seemed desirable, therefore, to attempt to determine, by a direct method, the precise numerical relation between the radiation and the convection from a wire heated by an electric current in an enclosure of air maintained at constant temperature, especially as an arrangement of apparatus recently employed by the author for the measurement of thermal conductivity was admirably adapted tor the purpose.

II. Experimental Procedure.

The wire or rod RR (*see* Figure) was supported in the middle of an enclosure of 5 cm. diameter, consisting of a brass water or steam jacket, JJJJ. One end of the wire, of slightly conical shape, was inserted in a hole bored in a solid copper cylinder, C, which fitted tightly into a hollow copper cylinder. Around the latter was wound 3 metres of pure platinum wire, gauge 30, single silk covered, and over this was another copper cylinder, AB. The end of the rod RR was raised to a temperature, V, above that of the enclosure by sending an electric current through the platinum coil. The temperatures of the hot end of the wire and of the enclosure were given by two platinum thermometers Pt_1 and Pt_2 respectively. After allowing adequate time (an hour or more) for temperature conditions to become steady, the current C through the platinum coil, and the E.M.F. E at its ends were measured by means of a carefully calibrated potentiometer. The specimen wire or rod was then removed, and the current adjusted so as to keep $Pt_1 - Pt_2$ precisely the same as when the wire was in position. If the current and E.M.F. be now denoted by C′ and E′, it is clear that the heat H given to the wire in order to maintain the temperature of its extremity $V(=Pt_1-Pt_2)$ above that of the enclosure is given by $CE-C'E'$.

It has been shown in previous Papers (*loc. cit.*) that for a rod of given dimensions (perimeter p, cross-section q, length l) and thermal conductivity k, whose end is raised V^0 above the temperature of the enclosure,

$$h=\frac{H^2 \coth^2 \alpha l}{pqk\ V^2},$$

where $\alpha=\sqrt{hp/qk}$.

Hence, $h \propto H^2$,

or the heat h lost per second from a square centimetre of surface for 1°C. excess is proportional to the *square* of the total heat loss, the latter being measurable.

The following experiments were therefore carried out :—

1. The amount of heat H $(=CE)$ was determined that was necessary to raise the temperature of the hot end of a brass rod a given amount V (about 10°C.),

(*a*) With the surface of the rod in its usual state—*i.e.*, slightly soiled by its exposure to the air,

(*b*) With the surface of the rod lightly and evenly coated with a dead-black varnish (an aniline dye dissolved in amyl acetate),

(*c*) With the rod removed.

2. A "Leslie cube" of 20 cm. edge was constructed of brass, and one of its faces was evenly coated with the same dead-black varnish as was employed in experiment (1) (*b*). The cube having been filled with water at a temperature a few degrees above that of the room, the relative "emissive powers" of the "metallic" and "black" surfaces were determined by means of a thermopile in connection with a low resistance galvanometer. (It was considered preferable to use a thermopile in preference to (say) a bolometer, since the former is steadier, and in addition, measures the total emission of all wave-lengths.)

Now, $$h_1/h_2 \text{ or } H_1^2/H_2^2=\frac{CE-C'E'}{C_1E_1-C'E'},$$

where

C, E are the current and E.M.F. when the rod is "black."
C_1 E_1 ,, ,, ,, ,, ,, ,, "bright."
C' E' ,, ,, ,, ,, ,, ,, removed.

Let $$H_1^2=aH_2^2,\ i.e.,\ h_1=ah_2, \tag{1}$$

as given by the first set of experiments.

Also let c=heat lost by convection in each case (assumed equal for both surface conditions of the rod).

Let r_1/r_2 be the measured ratio of amounts of heat lost by radiation from "black" and "bright" surfaces, as given by the second set of experiments, and suppose

$$r_1=br_2. \tag{2}$$

Hence, from (1) $$c+r_1=a(c+r_2). \tag{3}$$

From (2) and (3) $$\frac{r_2}{c}=\frac{a-1}{b-a}, \tag{4}$$

and $$\frac{r_1}{c}=\frac{b(a-1)}{b-a}. \tag{5}$$

Also $$\frac{r_2}{h_2}=\frac{r_2}{c+r_2}=\frac{a-1}{b-1}, \tag{6}$$

and $$\frac{r_1}{h_1}=\frac{r_1}{c+r_1}=\frac{b(a-1)}{a(b-1)}. \tag{7}$$

Equations (4) and (5) give at once the ratio of radiation to convection from the wire or rod when "bright" and "black" respectively, while (6) and (7) give the corresponding ratios of "radiation loss" to "total loss" of heat.

III. Experimental Results.

1. *Total Losses of Heat from Wire.*—Experiments were conducted with various wires, and employing different excesses of temperature. The rod (or wire) being put in position, and the current turned on and left until the steady state was reached, readings of C, E, Pt_1 and Pt_2 were obtained. The rod was then lightly varnished with the dead-black solution, without being moved from its position. After allowing sufficient time, the same measurements were again made. These operations were usually repeated two or three times to ensure consistent results. The rod was then removed, and C and E again determined, the excess of temperature, V $(=Pt_1-Pt_2)$, being kept

constant throughout. The following observations were made in the case of a brass rod :—

Brass Rod : Diameter, 3 mm. ; length, 30 cm.

(*a*) *Jan.* 16, 1915 : Pt_1, 17·12°C. ; Pt_2, 12·18°C. ; "V," 4·94°C.

	Black.	Bright.	Rod out.	h_1/h_2.
E	4,687	4,637	3,588	1·109
C	297·6	294·5	227·8	

$$\frac{h_1}{h_2}=\left(\frac{H_1}{H_2}\right)^2=\left(\frac{4{,}687\times297\cdot6-3{,}588\times227\cdot8}{4{,}637\times294\cdot5-3{,}588\times227\cdot8}\right)^2=1\cdot109.$$

(*b*) *Jan.* 9, 1915 : Pt_1, 19·01°C. ; Pt_2, 11·21°C. ; "V," 7·80°C.

	Black.	Bright.	Rod out.	h_1/h_2.
E	6,175	6,119	4,834	1·113
C	388·0	383·25	300·8	

(*c*) *Jan.* 18, 1915 : Pt_1, 20·34°C. ; Pt_2, 10·05°C. ; "V," 10·29°C.

	Black.	Bright.	Rod out.	h_1/h_2.
E	7,027	6,847	5,287	1·118
C	444·0	439·6	335·0	

An experiment with a *silver wire* gave the results :—

(*d*) *Jan.* 27, 1915: Diameter, 1 mm. ; length, 35 cm.

Pt_1, 23·29°C. ; Pt_2, 12·98°C. ; "V," 10·31°C.

	Black.	Bright.	Rod out.	h_1/h_2.
E	6,256	6,217	5,468	1·113
C	402·1	399·7	352·0	

In the case of a *copper wire*, the ratio h_1/h_2 was 1·109.

From the figures quoted it is evident that :—

(*a*) The increase in the emission of heat from a blackened rod or wire is about 11·5 per cent. ; in other words, the value of "a" in the equations derived above is 1·115.

(*b*) The effect of coating the rods with "dead-black" is about the same for all the metals examined, indicating that the amounts of heat lost by radiation from rods of different metals are the same, the rods being unblacked (*i.e.*, only slightly soiled by exposure to the air).

(*c*) The effect is, within the limits examined, independent of the diameter of the wire.

2. *Relative Losses of Heat by Radiation from "Metallic" and from "Dead Black" Surfaces.*—The "Leslie Cube" was filled with warm water, and the experiments conducted as already

described, as far away as possible from a fire or other source of heat. The thermopile employed consisted of 24 " elements " (Bi—Sb). A commutator was used in conjunction with the galvanometer, so that readings could be taken on both sides of the zero. Observations were made in the following order: " Black," " Bright," " Black," at equal intervals, and the average of the first and third compared with the second.

Radiation Experiments.

Dec. 29, 1914 : Distance of scale from galvanometer, 2 metres.			
First experiment : Temperature of " cube," 12°C. ; air temperature, 8°C. ; difference, 4°C.			
	Black surface.	Bright surface.	Ratio.
Deflection of galvanometer...	261 mm.	48·5 mm.	5·38 : 1
Second experiment : Temperature of " cube," 22°C. ; air temperature, 8°C. ; difference, 14°C.			
	Black surface.	Bright surface.	Ratio.
Deflection of galvanometer...	343 mm.	62·5 mm.	5·49 : 1
Third experiment : Temperature of " cube," 38°C. ; air temperature, 8°C. ; difference, 30°C.			
	Black surface.	Bright surface.	Ratio.
Deflection of galvanometer...	289 mm.	52 mm.	5·55 : 1
(The galvanometer was suitably shunted so as to give reasonable deflections in each case.)			

The results indicate that the relative amounts of radiation from " black " and " brass " surfaces are very nearly the same for all differences of temperature, the ratio increasing only slightly with increase of temperature excess. The approximate ratio is 5·5 : 1. That is, the value of " b " in equation (2) is 5·5.

Also " a " has been found=1·115.

Hence, from equation (4)

$$\frac{r_2}{c}=\frac{1{\cdot}115-1}{5{\cdot}5-1{\cdot}115}=0{\cdot}0262,$$

and from (5),

$$\frac{r_1}{c}=0{\cdot}144.$$

That is, the radiation in the case of the " bare " metal is 2·62 per cent. of the convection, and for the " blackened " metal is 14·4 per cent.

Also from (6) and (7),

$$\frac{r_2}{h_2}=\frac{a-1}{b-1}=2{\cdot}5 \text{ per cent.}$$

$$\frac{r_1}{h_1}=\frac{b(a-1)}{a(b-1)}=12{\cdot}6 \text{ per cent.}$$

Or, *of a total loss of heat of* 100 *parts*, 2·5 *are due to radiation, and* 97·5 *to convection* (*for a " bare " wire*). *If the wire is coated with " dead-black," the corresponding percentages are* 12·6 *and* 87·4.

IV. Experiments at Higher Temperatures.

The value of " h," the total loss of heat per second from 1 sq. cm. of surface of the wire for 1°C. excess, is considerably greater at 100°C. than at ordinary air temperatures. For example, the author obtained the values, " h " at 17°C. =0·000533, and at 100°C.=0·000634, for a wire 1 mm. in diameter. Lees,[*] in the case of a rod 5·85 mm. in diameter, obtained the values 0·000126, 0·000160 and 0·000200 at temperatures −155°C., −64°C. and 23°C. respectively; while the author, for a rod of about the same dimensions, found an increase from 0·000224 at 18°C. to 0·000265 at 100°C. It seemed of importance therefore to attempt to discover whether this increase of heat loss is due to radiation alone, or to convection alone, or in part to both causes. In an attempt to clear up this point as far as possible, similar experiments to those described in the preceding section were performed at a temperature 100°C. Rods and wires of various size and material were tested, the table on the next page showing some of the results obtained.

1. *Total Losses of Heat from the Wire at* 100°C.

It will be seen from the results given that :—

(*a*) The percentage increase of loss of heat from the blackened wire over that from the bare wire is over 20, this being nearly double that under similar circumstances at air temperatures.

(*b*) The increase is about the same for all the metals tested.

(*c*) The diameter of the rod seems to have little or no appreciable influence on the result.

2. *Radiation Experiments at Various Temperatures.*

The " Leslie Cube " was filled with boiling water, and readings taken as before of galvanometer deflections when the cone

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[*] C. H. Lees, " Bakerian Lecture," Roy. Soc. " Phil. Trans.," 1908.

(*a*) *Feb.* 4, 1915.—*Silver wire:* Diameter, 1 mm.; length, 35 cm.
Pt_1, 110·45°C.; Pt_2, 100·47°C.; "V," 10·18°C.

	Black.	Bright.	Wire out.	h_1/h_2.
E	7,535	7,452	6,562	1·202
C	390·4	386·4	340·7	

(*b*) *Feb.* 4, 1915.—*Copper wire:* Diameter, 1 mm.; length, 35 cm.
Pt_1, 110·63°C.; Pt_2, 100·47°C.; "V," 10·16°C.

	Black.	Bright.	Wire out.	h_1/h_2.
E	7,530	7,445	6 562	1·209
C	390·1	386·0	340·7	

(*c*) *Feb.* 8, 1915.—*Brass rod:* Diameter, 3 mm.; length, 30 cm.
Pt_1, 110·30°C.; Pt_2, 100·07°C.; "V," 10·23°C.

	Black.	Bright.	Rod out.	h_1/h_2.
E	8,570	8,390	6,517	1·213
C	443·0	435·0	338·5	

(*d*) *Feb.* 9, 1915.—*Bismuth rod:* Diameter, 6 mm.; length, 10 cm.
Pt_1, 110·00°C.; Pt_2, 99·89°C.; "V," 10·11°C.

	Black.	Bright	Rod out.	h_1/h_2.
E	7,643	7,546	6,475	1·214
C	396·9	391·5	336·3	

of the thermopile was placed at a fixed distance in front of (*a*) the metallic face, (*b*) the dead-black face of the cube. The readings were continued as the temperature of the water fell, this process being assisted by the addition from time to time of cold water. The galvanometer was suitably shunted at the various temperatures, so as to give readings on about the same part of the scale in each case. Cubes of brass and of "tinned iron" were employed, and gave results which did not differ materially from each other. Below are given readings in the case of the "tinned iron" cube:—

Radiation Experiments.

Feb. 11, 1915: "Tinned iron" cube, with one face dead-black.
Temperature of air, 13°C.; distance of galvanometer from scale, 2 metres.

Temperature of cube.	Deflection in millimetres.		Ratio.
	Black surface.	Metal surface.	
94°C.	433	82	5·28 : 1
65°C.	297	55·5	5·35 : 1
43°C.	206	39	5·29 : 1
32°C.	157	31	5·06 : 1
23·5°C.	220	43	5·11 : 1

Comparing these results with those previously given for a brass cube, it appears that the different metallic surface has very little influence on the result. Again, the ratio of emission of heat from the black surface to that from the metallic surface is very nearly the same at temperatures near 100°C. as at air temperatures. There is evidence, however, that this ratio (*i.e.*, the value of " b " of equation 2) increases slightly as higher temperatures are reached. This makes the value of " b " at 100°C. (for *brass*) 5·75—*i.e.*, 5 per cent. higher than at air temperatures. Also the value of " a " (from experiments 1 above) is 1·21.

Substituting these results in equations (4) and (5) we obtain :

$$\frac{r_2}{c}=\frac{a-1}{b-a}=\frac{0\cdot21}{4\cdot54}=4\cdot6 \text{ per cent.},$$

$$\frac{r_1}{c}=\frac{b(a-1)}{b-a}=26\cdot1 \text{ per cent.},$$

or the radiation from the bare wire at 100°C. is 4·6 per cent. of the convection, or 4·4 per cent. of the total loss of heat ; while that from the " black " wire is 26·1 per cent. and 20·7 per cent. respectively.

Also, from (6) and (7), *of a total loss of heat of* 100 *parts at* 100°*C.*, 4·4 *are due to radiation, and* 95·6 *to convection* (*for a " bare " wire*). *If the wire is coated with " dead-black," the corresponding percentages are* 20·7 *and* 79·3.

Not only, therefore, is the total amount of heat emitted greater at higher temperatures, but the proportion of radiation is greater. The percentage radiation loss of the total loss of heat rises from 2·5 per cent. to 4·4 per cent. for a rise of temperature from 12°C. to 100°C. For the same interval of temperature the increase in the total loss of heat is about 20 per cent. Hence, the radiation loss from a wire is increased in the proportion of 2·1 : 1 for the increase in temperature from 12°C. to 100°C., the excess of temperature of the wire being 10°C.

If we could assume the " Fourth Power " Law for this radiation loss, we should have (for an excess of 10°C. in each case)—

$$\frac{R_{12}}{R_{100}}=\frac{295^4-285^4}{383^4-373^4}=\frac{1}{2\cdot21.}$$

That is, the radiation loss at 100°C. would be (for " full " radiation) about 2·2 times that at 12°C., a result close to that obtained by experiment, which gave 2·1 : 1. Of course, this only indicates that the *ratio* of the radiations from the wire at the two given temperatures is the same as the ratio of the "full" radiations at corresponding temperatures. It is clear, however, that the greater portion (nearly 90 per cent.) of the increase in the loss of heat from a wire at 100°C. above that at 12°C. is due to increased convection.

V. Discussion of Results.

It is interesting to compare the foregoing experimental results with those obtained from application of various radiation formulæ that have been proposed. For example, L. V. King (*loc. cit.*) has quoted a formula by Lummer and Kurlbaum for the radiation loss from a platinum surface, $e=0{\cdot}514\,(\theta/1{,}000)^{5\cdot2}$ watts per square centimetre per 1°C. excess.

Taking the absolute temperature of the enclosure as 290°C. and that of the wire as 300°C., this gives

$e=0{\cdot}000038$ cals. per square centimetre for 10°C. excess.

Thus, for a wire of 1 mm. diameter, where the total loss of heat per square centimetre for 10°C. excess is 0·00533, we have

$$\frac{\text{Radiation loss}}{\text{Total loss}}=0{\cdot}7 \text{ per cent.}$$

In the case of a rod of 6 mm. diameter, the "total loss" under the same circumstances is only 0·000224, and here the loss by radiation would be 1·7 per cent. of the total loss. (The experiments of the present research give 2·5 per cent. in each case.)

Again, applying Stefan's "Fourth Power" law for full radiation, $H=\sigma(\theta^4-\theta_0^4)$, and taking $\theta=300$°C., $\theta_0=290$°C., and $\sigma=5{\cdot}35\times10^{-5}$ (ergs) (Valentiner, A. d. P., 1910),

$H=0{\cdot}001308$ cals. per square centimetre for 10°C. excess at air temperatures. (At 100°C. this would be doubled—*see* Section IV.)

Now, the present research gives (for a *black* surface in a *brass* enclosure),

12·6/100 of 0·00533=0·00067 calories radiated for 10°C. excess from a wire 1 mm. diameter—*i.e.*, about a half of what is required by Stefan's law. This is probably accounted for by the brass enclosure, and possibly also, partly, from the "black" varnish used being not exactly a "full" radiator.

It is noticeable in the experimental results of the present Paper that the proportion of radiation to convection is almost precisely the same for wires of all diameters. As the total "h" decreases with increase of diameter of the wire, this points to a decrease of actual radiation per square centimetre as the diameter increases. I am not aware of any definite reason for this, but there is no doubt of the fact in the present arrangement of apparatus. It has been suggested that a considerable proportion of the heat lost from the wire when it is "blacked" may possibly be due to the increase of thickness of the "wire" caused by the coat of varnish. This is not very likely, however, for the coating was exceedingly thin, and, in addition, the thermal conductivity of the varnish is certainly very many times less than that of the metallic wire.

In conclusion, it is apparent that—at any rate in the case of a wire heated within an enclosure of limited dimensions—the radiation from a wire plays a more important part than has been supposed by some workers. On the other hand this loss is not sufficient, at ordinary temperatures at all events, to interfere seriously with the validity of Newton's "Law of cooling," unless the temperature of the wire is raised considerably above that of the enclosure.

Summary.

The object of the experiments here recorded was to determine the numerical relation between the radiation and the convection losses from a heated metallic wire or rod placed in a gas at constant temperature. The method consisted in (1) measuring the amount of heat required to maintain the temperature of the wire a given amount (about 10°C.) above that of the surrounding gas, the surface of the wire being (*a*) coated with a dead-black varnish, (*b*) uncoated; (2) comparing the radiations from two surfaces exactly similar to (*a*) and (*b*) by means of a thermopile.

It is shown that if the total heat lost from unit surface of the wire is "a" times greater from a "black" wire than from a "bare" one, while the radiation from the black surface is "b" times more that from the unblacked surface, then

$$\frac{r_2}{c} = \frac{a-b}{a-1}, \text{ and } \frac{r_1}{c} = \frac{b(a-b)}{a-1},$$

where r_2, r_1, are the radiations from "black" and "bare" surfaces respectively and c is the convection.

The experiments indicate that of 100 parts of "total heat" lost from a wire at air temperatures, 2·5 consist of radiation for a bare wire, and 12·6 for a "black" wire. At 100°C., these percentages become 4·4 and 20·7 respectively. The 20 per cent. increase in "total loss" of heat from 17°C. to 100°C. is thus caused chiefly by increased convection.

DISCUSSION.

Dr. H. **Borns** asked if the author had tested the validity of the assumption that the convection was independent of the nature of the surface of the wire.

Mr. F. E. **Smith** asked why the platinum thermometer employed to give the temperature of the enclosure was placed inside it. There would be a temperature gradient between the wire and the enclosure and the thermometer could not give the correct temperature of the latter.

Dr. W. **Eccles** asked if the size of the enclosure affected the results. He had once studied the effects of convection in lifting the boom of a small micro-balance. The convection was due to the heating effect of the current in the instrument and the magnitude of the effect depended on the size of the enclosure.

Dr. A. **Russell** welcomed the author's work as being the first experimental attempt to determine the proportion of heat lost by radiation and convection. In early discussions on the heating of wires prominence was given to the nature of the surface which they should have to make the heat lost as great as possible. It appeared from the author's results that practically all the heat was lost by convection, and so whether the surface was blackened or not was not of much consequence. With different diameters of wire, did the convection loss vary inversely as the square root of the diameter ? It should do so if the convection currents were uniform. Did the amount of heat radiated per unit area depend on the curvature ? From these results it seemed to decrease as the radius was increased.

Mr. J. H. **Brinkworth** (communicated remarks) referred to some results of his experiments by the continuous flow method on the specific heat of steam ("Phil Trans.," A. 535, pp. 434 and 436). In these measurements the heat loss from the calorimeter was varied by altering the pressure of the air in the sheath surrounding the flow tube. The heat loss per degree per centimetre length of flow tube, when the sheath was evacuated as perfectly as possible—in which case radiation alone occurred —lies between 5 and 10 per cent of the loss when the pressure in the sheath was about 1 mm. of mercury.

Dr. **Barratt**, in reply, said he did not quite see how to verify experimentally that the convection was the same with the two kinds of surface employed. He thought that if the surface was smooth in each case the convection loss was bound to be the same. The classic experiments of Dulong and Petit, however, led to the conclusion that the cooling effect of the gas was quite uninfluenced by a difference of surface of the hot body. With regard to the position of the second platinum thermometer, he had found that when it was placed about half-way along and below the wire it gave the temperature of the ascending gas, and it is this temperature that determines the rate of loss of heat by convection. The comparative thermal capacity of the jacket was so great that this temperature was almost exactly equal to that of the jacket. He had not tried the effect of different sized enclosures, and the results given are, of course, only strictly applicable to the particular case investigated. With wires of different diameters the total heat loss per square centimetre decreased as the diameter of the wire increased, but he had not seen whether or not the square-root law mentioned by the Chairman held for the convection loss. Mr. Brinkworth's results are important as showing that convection losses are predominant down to such a low pressure as 1 mm. of mercury.

II. *The Magnitude of the Thermal Resistance introduced at the Slightly Conical Junction of Two Solids, and its Variation with the Nature of the Surfaces in Contact. By* THOMAS BARRATT, *A.R.C.S., D.Sc.*

RECEIVED JUNE 22, 1915.

1. *Introduction and Description of Apparatus.*

IN Papers on the thermal conductivity of solids, recently published,* it was necessary to determine the fall of temperature caused by the thermal resistance at the joint where the conical extremity of a solid rod fitted, as accurately as possible, into a hole bored in a solid copper cylinder. In the investigation there recorded the only case treated was where the joint was of brass-copper, and it was assumed that the magnitude of the effect would be the same under similar conditions for other solids. In order to test the validity of this assumption, similar experiments have been conducted to determine the variation, if any, of the thermal resistance with the nature of the surfaces in contact.

One end of a rod of brass, RR (*see* Figure on p. 2 in previous Paper), fitted accurately into a slightly tapering conical space bored in a solid cylinder of copper, C, which was enclosed in a hollow cylinder of thin copper. The latter could be heated to any required temperature (recorded by a platinum thermometer, Pt_1), by means of a coil of single silk covered pure platinum wire, gauge 30, which was closely wound round it. This coil again was covered by another cylinder of copper, AB, whose thickness increased from zero at one end to about 2 mm. at the end into which the brass rod RR was fitted.

The product of readings of the current (C) and E.M.F. (E) at the ends of the platinum coil round the copper cylinder gave the amount of heat necessary to maintain the temperature of the copper block C any given amount V above that of the constant temperature enclosure, the latter consisting of a water or steam-jacket, JJJJ, within which the whole apparatus was kept. The temperature of this enclosure was given by a second platinum thermometer Pt_2 A hollow cone of very thin brass was made to fit as accurately as possible the end of the rod, so as to form a "double joint," thus doubling the thermal resistance effect. Readings were then taken of the amounts of heat necessary to maintain a given temperature difference, V ($=Pt_1-Pt_2$), between the copper block and the enclosure:—

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* T. Barratt, Phys. Soc. "Proc." XXIX, V., August 15, 1914; and XXVII, I, December 15, 1914.

1. With the rod and hollow cone in position,
2. With the rod only in position,
3. With the rod and cone both removed.

If the difference of the amounts of heat in (2) and (3) be denoted by H, and that between (1) and (3) by H_1, it was shown in the former of the two Papers referred to above that

$$\frac{V}{V_1}=\frac{H}{H_1}=\frac{CE-C'E'}{C_1E_1-C'E'},$$

where V is the excess of temperature of the *copper block* over that of the enclosure.

V_1 the excess of temperature of the *hot end of the rod* over that of the enclosure.

H and H_1 the amounts of heat given to the rod with the cone "in" and "out" respectively.

C, E the current and E.M.F. with rod in and cone out.

C_1, E_1 the current and E.M.F. with rod and cone both in.

C', E' the current and E.M.F. with rod and cone both out.

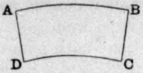
Measurements made with the brass cone had indicated that the percentage fall of temperature at the junction was constant, within the errors of experiment, both for different excesses of temperature (V) and for actual temperatures (17°C. and 100°C.) of the enclosure.

The value of H/H_1 or V/V_1 was 1·025 as given by the mean of several concordant experiments.

II. Experiments with Different Surfaces in Contact.

This abrupt fall of temperature at a junction is no doubt mainly due to the film of air that must exist between the two surfaces in contact. In order to investigate the effect for other metals similar experiments were conducted employing the same apparatus, but with cones of various substances—*e.g.*, copper, aluminium, zinc, platinum, &c. In some experiments the end of the brass rod was coated with a very thin layer of copper, deposited electrolytically, this procedure having been followed in every case in the original experiments on the conductivity of metals. No difference whatever could be detected in the results, whether the end were "coppered" or not.

The "cones" employed were of thickness only one-tenth of a millimetre and were made by cutting out from the metal foil part of a sector of the exact size required, thus



and folding it over the conical end of the brass rod, so that AD lay alongside and just touching BC.

The usual procedure in a "full" experiment was as follows :

The end of the brass rod of diameter 3 mm., length 30 cm., was fitted tightly into the junction, the current C turned on, and the apparatus left for one or two hours for temperature conditions to become steady. Readings were then taken of C, E, Pt_1 and Pt_2. The rod was quickly removed, one of the cones fitted to the end of it and replaced. When conditions were again steady (this requiring only a few minutes), C_1 and E_1 were read, after being adjusted to maintain V $(=Pt_1-Pt_2)$ the same as at first. The other cones were fitted successively in the same manner, C′ and E′ were obtained with rod and cone both removed, and the cones were again tested, this time in reverse order. The means of the values of C_1 and E_1 for each cone were calculated, and taken as the true readings. The whole experiment, once temperature conditions were steady, took about 2 to 2½ hours for the seven or eight cones, and it was usually found that very little variation of temperature occurred in that interval. Of course, the *difference* of temperature (Pt_1-Pt_2) was kept absolutely constant throughout.

Below are given the actual determinations in one of this series of experiments :—

December 31, 1914 : Brass rod, end "coppered," diameter 3 mm.
Temperature of "hot" end, 14·95°C. ; temperature enclosure, 6·56°C.

No cone.	Cu.	Pt.	Zn.	Ag.	Al.	Sn.	Pb.	Brass.	Rod out.
E, 6,027	5,995	5,986	5,986	5,989	5,983	5,973	5,970	5,970	4,559
C, 3,861	3,844	3,841	3,841	3,844	3,843	3,838	3,840	3,843	2,926

For copper cone, $V/V_1=H/H_1=(CE-C'E')/(C_1E_1-C'E')=9{,}939/9{,}705$ $=1{\cdot}024$, $=2{\cdot}4$ per cent. fall of temperature at the junction.

Similarly, as calculated from observations above, the results for other cones were as follows :—

Pt.	Zn.	Ag.	Al.	Sn.	Pb.	Brass.
1·029 ...	1·029 ...	1·026 ...	1·029 ...	1·037 ...	1·035 ...	1·035

The mean results of seven consecutive experiments were :—

Metal..........	Ag.	Cu.	Al.	Pb.	Sn.	Zn.	Pt.	Brass.
Fall of temp..	2·1%	2·1%	2·3%	3·1%	2·9%	2·7%	2·7%	3·0%

The mean percentage excess of V over V_1 for all the surfaces tested is thus very nearly 2·5 per cent., this being the value adopted in the Paper already referred to.

The value of V/V_1 is seen, however, to depend to some extent on the nature of the surfaces in contact. In fact, the thermal resistances at the junctions are found to be nearly in the same order as the reciprocals of the thermal conductivities (***k***) of the metal cones themselves. A comparison of "*k*" with the corresponding value of V/V_1 is given :—

Metal.	Ag.	Cu.	Al.	Zn.	Brass.	Pt.	Sn.	Pb.
"*k*"	1·006	0·918	0·480	0·265	0·260	0·166	0·155	0·083
V/V	2·1	2·1	2·3	2·7	3·0	2·7	2·9	3·1

III. Effect of "Coppering" the Joints, and of Smearing them with Olive Oil.

(*a*) It has been mentioned that no appreciable difference was observed in the value of V/V_1 (*i.e.*, of H/H_1) when the end of the brass rod was covered with a thin film of copper. To investigate this further, a brass rod of uniform diameter 3 mm. and length 35 cm. had both its ends turned down to exactly similar conical shape. Readings were then taken of the value of "H" (*i.e.*, CE) for a given temperature difference (V), when each end in turn was inserted in the copper block. The readings were alike to within 1 part in 1,000. One end was then "coppered" by electrolytic deposition, and the experiments repeated. The results were as follows :—

Brass end	CE=2,855
Coppered end	CE=2,852

indicating that the presence of the thin film of copper made no difference whatever to the thermal resistance at the junction.

(*b*) Several experimenters on thermal conductivity have smeared the junction of two metallic surfaces with grease or oil. This procedure was, therefore, tried, pure olive oil being employed. "H" was measured in the usual way, and then

"H" was determined when the joint was smeared with the olive oil. The results are given :—

January 11, 1915 : Pt_1, 14·63°C. ; Pt_2, 7·24°C. ; "V," 7·39°C.			
	Rod in, no oil.	Rod in, with oil.	Rod out.
Heat given	21,117	21,223	12,128

Hence, $H/H_1 = V/V_1 = 9{,}115/9{,}069 = 1{\cdot}005$.

That is, the heat given to the rod is 0·5 per cent. greater when oil is put on the joint. In other words, the thermal resistance at the junction is 0·5 per cent. less *with* olive oil than without.

(In the original research, oil was not used at the joints, because it hindered necessary quickness in manipulation, and because of the danger of alteration of surface emission of heat if any oil were left on the rod itself, or if it oozed out of the joint.)

IV. Experiments with Rods of Low Thermal Conductivity.

In the research on the thermal conductivity of badly conducting solids (*loc. cit.*), the substances experimented upon were in the form of cylindrical rods about 6 mm. diameter. The thermal resistance at the junction in this case was not measured but was assumed to be the same for all the solids investigated as for a pure bismuth rod, when they were under precisely the same conditions. The thermal conductivity of the bismuth being assumed, it was unnecessary exactly to measure the fall of temperature at the joint, provided it could be assumed equal for all the solids examined. In order to test the truth of this assumption, similar experiments to those described above were carried out with the original bismuth rod. Cones of thin paper, tinfoil, copper, &c., were made to fit the joint, and the value of H/H_1 determined in the usual way. The following results were obtained in one of these experiments :—

January 20, 1915 : Bismuth rod, diameter, 6 mm. ; length, 10 cm. ; Pt_1, 24·79°C. ; Pt_2, 14·04°C. ; "V," 10·75°C.			
	Paper cone.	No cone.	Copper plug (in place of rod).
E	6,626	6,648	5,610
C	414·15	405·0	351·5

This gives $V/V_1 = H/H_1 = 1{\cdot}019^* = 1{\cdot}9$ per cent. excess.

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* To obtain this result, 5 per cent. was added on to "H" and to "H_1," in order to account for the heat lost from the surface of the copper plug. The explanation of this correction has been given fully in one of the Papers mentioned above.

Similar experiments with a tinfoil cone gave $H/H_1=1{\cdot}008$ $=0{\cdot}8$ per cent. excess. With a copper cone the thermal resistance at the junction was less than 0·5 per cent.

The results indicate that in the case of thicker rods of badly conducting material the fall of temperature at the junction is rather less than in the case of thin rods of comparatively high conductivity. This result is somewhat unexpected, but the probable explanation is that the air space at the junction (of almost molecular dimensions) has a relatively smaller effect than with the thinner rods of higher thermal conductivity. Even when a Paper surface is used, the relative thermal resistance at the joint is very small (less than 2 per cent.), in spite of its extremely low thermal conductivity. When a metallic surface is fitted to the joint, very little difference indeed can be detected in the amount of heat H flowing into the bismuth rod.

V. Interpretation of Results.

The true explanation of these results may be that the thermal resistance at similar junctions of two solids is constant, and *entirely* due to the film of air present. (That is to say, there is no certain indication of any phenomenon analogous to the fall of electrical potential at the junction of two dissimilar metals, where the nature of the metallic surfaces determines the magnitude of the effect.) In the case of a metallic wire of diameter about 1 mm., the influence of this film of air is relatively large. The presence of the very thin "cones" of various metals causes an additional thermal resistance, the magnitude of which is small if expressed in terms of "air," and which varies with the thermal resistance of the metal of which the cone is composed. The latter conclusion is most strongly supported by the experiments on the thicker rods of low thermal conductivity, where the influence of the paper cone of high "air" equivalent is much more marked than that of a metallic cone.

Taken as a whole, therefore, the results obtained in the present series of experiments justify the assumptions made in former Papers, viz. :—

1. That the thermal resistance at junctions of various metals of comparatively high conductivity and small diameter (about 1 mm.) is constant, and has a value of 2½ per cent.

2. That the thermal resistance at the junction of thicker rods (6 mm. diameter) of low thermal conductivity is rather

smaller, and does not depend on the material of which the rod is composed.

Summary.

The abrupt fall of temperature caused by the thermal resistance at the slightly conical junction of two solids has been examined, the method consisting in constructing a "double joint," thus doubling also the thermal resistance effect.

In the case of wires of small diameter, the fall of temperature was found to be 2½ per cent.; that is, the temperature of the "hot" end of the wire is 2½ per cent. lower than that of the copper block into which the end of the wire was fitted.

This percentage fall of temperature is practically the same at all temperatures of the enclosure (up to 100°C.), and is independent of the excess of temperature of the end of the wire above that of the enclosure (at any rate, up to 10°C. or 12°C.).

For wires of greater diameter (6 mm.) the resistance is rather less than for smaller wires.

The thermal resistance is probably entirely due to the thin film of air that must exist at the joint between the wire and the copper block.

The experiments have been carried out at the Wandsworth Technical Institute, and my thanks are due to the Principal and Governors thereof for their kind interest in the work.

III. *On the Determination, by the Method of Diffusive Convection, of the Coefficient of Diffusion of a Salt Dissolved in Water.* By ALBERT GRIFFITHS, *D.Sc.* (*Manc.*), *A.R.C.S.* (*Lond.*), *Head of Physics Department, Birkbeck College, London.*

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§ 1. Theory of the method.
§ 2. Notes on Earlier work and Difficulties.
§ 3. Details and Dimensions of the Apparatus.
§ 4. Method of Conducting the Experiment.
§ 5. References to Discarded Forms of Apparatus.
§ 6. Specimen-results with the Reservoir-method of introducing index.
§ 7. Experiments and Results with the Tap-plug Method of Introducing Index.

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§ 1. *Object and Theory of the Method.*

THE object of the research was to develop a method of determining the coefficient of diffusion of a salt dissolved in water which involves the application of purely physical, as distinct from chemical, measurements which possesses the characteristic that all measurements are made after the attainment of the steady state of diffusion, and which promises to possess the advantage that there shall be no disturbance of the apparatus, internally or externally, during the period of crucial observations.

Some of the essential features of the apparatus are sketched in Fig. 1.

A and B may be called the diffusion-tubes. Their upper ends terminate in cylindrical vessels which are connected together by the long capillary tube CD. The cylindrical vessels are each connected by two vertical tubes to vessels E and F. T is a large glass tank. The whole apparatus is first filled with water, and then the water in the tank is replaced by a solution of the substance whose coefficient of diffusion is desired. In general a flow of water takes place along the capillary; and if the rate of flow, when the steady state is attained, be known, it is possible to calculate the coefficient of diffusion of the salt.

Let it be assumed that the area of the cross-section of the tube A is the same as the area of the cross-section of the tube B.

Let h_1=the height of the top of the tube B above the top of the tube A.
h_2=the height of the bottom of B above the bottom of A.
L_1=length of tube A.
l_1=distance from the top of A to a point in the tube A.
L_2=length of tube B.
l_2=distance from the top of B to a point in the tube B.
r=radius of capillary tube.

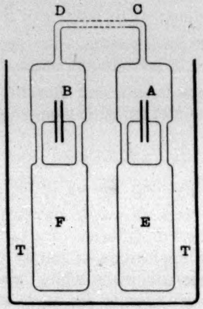

FIG. 1.

λ=length of capillary tube.
η=coefficient of viscosity of water.
q=ratio of area of cross-section of A or B to that of the capillary.
v_1=upward linear velocity of water at the top of the tube A.
v_2=downward linear velocity of water at the top of the tube B.
V=average linear velocity of water along the capillary.
ρ=density of solution.
n=concentration of solution in grammes per cubic centimetre.
N=concentration of solution in the tank.

c_1=quantity of salt transmitted per second by the combined action of diffusion and convection across unit area of the tube A.

c_2=corresponding quantity for tube B.

k=coefficient of diffusion of the salt.

It is assumed that $\rho=1+an$, where a is a constant depending on the salt dissolved.

Let $b=1-a$.

Since, when the steady state is attained, the water crosses each section of the tube B at the same rate, it follows that

$$v_2=v''(\rho-n_2)=v''(1-bn_2),$$

where v'' is the downward velocity of the solution at a point in the tube where the concentration is n_2.

Similarly, under the same conditions, the mass of salt transmitted by the compound operation of convection and diffusion through each cross-section of B is constant, and

$$-v''n_2+\frac{kdn_2}{dl_2}=c_2\,;$$

whence
$$-\frac{v_2n_2}{1-bn_2}+\frac{kdn_2}{dl_2}=c_2.$$

A solution of the last differential equation is

$$\frac{-bn_2}{v_2-bc_2}+\frac{v_2}{(v_2-bc_2)^2}\log_e\frac{(v_2-bc_2)n_2+c_2}{c_2}=\frac{l_2}{k}\quad . \quad . \quad . \quad (1)$$

and
$$\frac{bn_1}{v_1+bc_1}-\frac{v_1}{(v_1+bc_1)^2}\log_e\frac{c_1-(v_1+bc_1)n_1}{c_1}=\frac{l_1}{k}\quad . \quad . \quad . \quad (2)$$

The head, measured in centimetres of water, due to the liquid in the tube B, equals

$$\int_0^{L_2}\rho dl_2=\int_0^{L_2}(1+an_2)dl_2=L_2+a\int_0^{L_2}n_2dl,$$
$$=L_2+a(NL_2-\int_0^N l_2dn_2).$$

Equation (1) gives l_2 as a function of n_2, and the integration shows that

$$\int_0^{L_2}\rho dl_2=L_2+aNL_2-a\left[kv_2\left\{\frac{(v_2-bc_2)N+c_2}{(v_2-bc_2)^3}\right\}\log\frac{(v_2-bc_2)N+c_2}{c_2}\right.$$
$$\left.-\frac{bkN^2}{2(v_2-bc_2)}-\frac{kv_2N}{(v_2-bc_2)^2}\right].\quad . \quad . \quad . \quad . \quad (3)$$

In a similar manner it can be proved that

$$\int_0^{L_1}\rho\, dl_1=L_1+aNL_1-a\left[kv_1\left\{\frac{c_1-(v_1+bc_1)N}{(v_1+bc_1)^3}\right\}\log_e\left\{\frac{c_1-(v_1+bc_1)N}{c_1}\right\}\right.$$
$$\left.+\frac{bkN^2}{2(v_1+bc_1)}+\frac{kv_1N}{(v_1+bc_1)^2}\right]. \quad . \quad (4)$$

Let z=the head in centimetres of water required to drive the water along the capillary with average linear velocity V, calculated from Poiseuille's equation.

Then

$$\int_0^{L_2}\rho\, dl_2+h_2(1+aN)-\int_0^{L_1}\rho\, dl_1-h_1-z=0. \quad . \quad . \quad . \quad (5)$$

It can easily be proved that the increase in the volume of a weak solution of the salt due to the addition of 1 gramme of the salt is numerically equal to b.

The volume-flow downwards through the upper section of the tube B is equal to the volume-flow along the capillary plus the increase in volume of the water of weak solution above B due to the salt transmitted along B.

Let S=the area of cross-section of tube A or B.

s=the area of cross-section of the capillary.

Then $$v_2S=Vs+bc_2S \text{ or } v_2=\frac{Vs}{S}+bc_2.$$

Let $$v=\frac{s}{S}V=\frac{V}{q}.$$

It may be mentioned that v is the velocity there would be in the diffusion tubes if b equalled zero. It is approximately equal to the actual velocity of the liquid in the diffusion tubes.

Then $$v_2=v+bc_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Similarly, $$v_1=v-bc_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Substituting these values of v_1 and v_2 in (1), (2), (3) and (4), and introducing limiting values when need be, the equations become

$$\frac{bN}{v}-\frac{v-bc_1}{v^2}\log_e\left\{1-\frac{vN}{c_1}\right\}-\frac{L_1}{k}=0. \quad . \quad . \quad . \quad (8)$$

$$-\frac{bN}{v}+\frac{v+bc_2}{v^2}\log_e\left\{\frac{1+vN}{c_2}\right\}-\frac{L_2}{k}=0\ .\quad .\quad .\quad .\quad (9)$$

$$\int_0^{L_1}\rho dl=L+aNL-ak\left\{\frac{(v-bc_1)c_1\left(1-\frac{vN}{c_1}\right)\log_e\left(1-\frac{vN}{c_1}\right)}{v^3}\right.$$
$$\left.+\frac{bN^2}{2v}+\frac{(v-bc)N}{v^2}\right\}.\quad .\quad .\quad .\quad .\quad (10)$$

$$\int_0^{L_2}\rho dl=L+aNL-ak\left\{\frac{(v+bc_2)c_2\left(\frac{1+vN}{c_2}\right)}{v^3}\log_e\left(1+\frac{vN}{c_2}\right)\right.$$
$$\left.-\frac{bN^2}{2v}-\frac{(v+bc_2)N}{v^2}\right\}.\quad .\quad .\quad .\quad (11)$$

In one calculation the value of k was determined as follows :

An approximate value of k was assumed, and c_1 and c_2 were found by Horner's method. The values of

$$\int_0^{L_1}\rho dl \quad \text{and} \quad \int_0^{L_2}\rho dl$$

were then found, and the results substituted in equation (5). The value of the left-hand side of (5) did not equal zero. Another value of k was then taken and calculations made once more of the value of the left-hand side of (5). The value again did not equal zero. The true value of k was found by extrapolation.

When $L_1=L_2=L$, and $h_1=h_2=h$, as was the case in the experiments to be described, it can easily be proved that equation (5) simplifies to

$$\frac{ak}{v}\left\{(c_1+c_2)\frac{L}{k}+bN^2-2N\right\}+haN-z=0.\quad .\quad .\quad (12)$$

A more convenient form of equation (8) for purposes of calculation is

$$\varphi(c_1)=bNv-(v-bc_1)\log_e\left(1-\frac{vN}{c_1}\right)-\frac{L}{k}v^2=0.\quad .\quad .\quad (13)$$

and a more convenient form of (9) is

$$\varphi(c_2)=-bNv+(v+bc_2)\log_e\left(1+\frac{vN}{c_2}\right)-\frac{Lv^2}{k}=0\ .\quad .\quad (14)$$

On account of the utility of the functions in Horner's method of solving an equation by successive approximation it may be mentioned that

$$\varphi'(c_1)=b\log_e\left(1-\frac{vN}{c_1}\right)-\frac{Nv}{c_1^2}\,\frac{(v-bc_1)}{1-\dfrac{vN}{c_1}}, \quad . \quad . \quad . \quad . \quad (15)$$

and that

$$\varphi'(c_2)=b\log_e\left(1+\frac{vN}{c_2}\right)-\frac{Nv}{c_2^2}\,\frac{(v+bc_2)}{1+\dfrac{vN}{c_2}}. \quad . \quad . \quad . \quad . \quad (16)$$

An approximate value of k is first assumed, and c_1 and c_2 are determined by Horner's method. After a little experience approximate values of c_1 and c_2 may easily be obtained. At the commencement, approximate values of c_1 and c_2 are given by equations derived from (13) and (14) by putting b equal to zero. Precise values of c_1 and c_2 having been obtained, their values are substituted in equation (12).

The value of the left-hand side of (12) will not, in general, equal zero. Another value of k is then taken, c_1 and c_2 are determined once more, and the value of the left-hand side of (12) is again calculated. The true value of k is found by extrapolation.

Semi-Empirical Formulæ.—The calculations described in the preceding section are very tedious. The author some years ago did some work on the assumption that $d=1+n$; that is, on the assumption that $a=1$ and $b=0$.

The results then obtained are substantially true, in spite of the appreciably large value of b in the case of potassium chloride.

Let v_0 be the velocity of the water at the top of a diffusion tube. It can easily be proved that the velocity of the liquid at the bottom of the tube is $v_0 \div (1-bN)$. The mean of the two velocities is

$$v_0\frac{1-\dfrac{bN}{2}}{1-bN} \quad \text{or} \quad \frac{v_0}{1-\dfrac{bN}{2}}$$

approximately. By modifying the result which would be obtained on the simple assumption that $d=1+n$, and replacing

v_0 by $v\div\left(1-\frac{bN}{2}\right)$, the author has obtained the empirical formula

$$\varphi(x)=\frac{h}{L}-\frac{z}{aNL}, \tag{17}$$

where

$$\varphi x=\frac{e^x+1}{e^x-1}-\frac{2}{x}=\frac{\cosh\frac{x}{2}}{\sinh\frac{x}{2}}-\frac{2}{x}. \tag{18}$$

and

$$x=\frac{vL}{\left(1-\frac{bN}{2}k\right.}. \tag{19}$$

It is comparatively easy to solve (17) by a method of interpolation ; having found (x), k follows by means of (19).

The empirical formula (17) gives k, in its application to the apparatus described in this Paper, to an accuracy of one-tenth per cent. ; and the author is inclined to think that it will apply to apparatus of considerably different dimensions.

Where the dimensions are those of the apparatus described in this Paper, (17) may be shown to be approximately equivalent to

$$k=\frac{vL\left\{1-\frac{3}{5}\left(\frac{h}{L}-\frac{z}{aNL}\right)^2\right\}}{6\left(1-\frac{bN}{2}\right)\left(\frac{h}{L}-\frac{z}{aNL}\right)} \tag{20}$$

This also gives k to an accuracy of about one-tenth per cent. When the ratio of h to L is small and z is negligible (20) becomes

$$k=\frac{vL^2}{6h\left(1-\frac{bN}{2}\right)}. \tag{21}$$

§ 2. *Notes on Earlier Work and Difficulties.*

In 1904 the author studied experimentally the relation between the velocity of the extremity of a solution of methyl violet along a capillary tube which originally contained water and the average rate of flow along the capillary ; and he determined the coefficient of diffusion of copper sulphate. The result was approximately correct, but the indication of the speed given by the methyl violet was not sufficiently consistent to make the result of value. About this time the author's colleague, Mr. B. W. Clack, commenced some careful and painstaking work with potassium and sodium chloride, and the author thought it wise to work with these solutions. In the sequel the change of solution proved to be a source of increased difficulty. In 1910 the author developed a precise method of measuring the rate of flow along a capillary tube.*

Numerous experiments were performed with the diffusion-apparatus. The flow was always in the right direction, and was as a rule fairly constant during the journey of an index; but the flow was never the same for two experiments in succession until 1914, *when a radical change was made in the method of introducing the index.*

In 1911† it was discovered that fungoid growths formed in the capillary tube; but even after the elimination of the growths by the addition of a trace of a copper salt no two successive journeys gave the same speed.

Attention was finally directed to the method of introducing the index. This introduction was originally effected by a reservoir of about 30 cubic cm. capacity interposed in the course of the capillary tube, and in introducing the index the water in the reservoir was replaced by fresh water. The earlier forms of apparatus were designed so that the journey was completed in a week or less; but, by a fortunate chance, an apparatus was made in which the journey of the index lasted for a fortnight. It was discovered that the introduction of the fresh water always disturbed the flow, and that the disturbance was often appreciable for a week. Under similar conditions, the rate of flow during the second week attained to 5 or 10 per cent. the same value in successive experiments. *The author wishes to call special attention to this disturbance.* The head between the extremities of the capillary tube is, as a rule, of the order of one thousandth of a centimetre of water, and it is obvious that a slight resistance will create a large temporary disturbance. It may be mentioned that there is a disturbance even if the water that is taken out of the reservoir is returned to it. The author suspects the cause of the disturbance to be some lack of homogeneity in the water at the ends of the capillary tubes in the reservoir. The phenomenon may be due to soluble impurities or to variations in the number of colloidal particles suspended in the water. Further research is desirable with apparatus not complicated by diffusion.

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* "Proc." of Phys. Soc., Vol. XXIII., Part III., pp. 190-197. 1911.

† "Proc." of Phys. Soc., Vol. XXIV., Part V., pp. 350-357. 1912.

In the latest experiments a method of introducing an index has been employed which involves the substitution of only a small fraction of a cubic centimetre of water by a weak solution of uranine. The final form of the device was due to the author's wife. It involves the use of an ordinary glass tap-plug, and is described in a separate Paper. With it, successive indexes have approximately the same speed.

§ 3. *Details and Dimensions of the Apparatus.*

The measurements given are those used in the calculations, and they are not to be regarded as precise to the last significant figure.

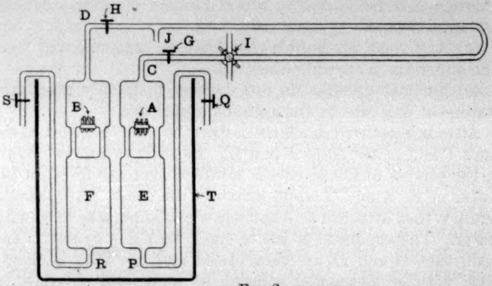

FIG. 2.

They are usually the result of averages, and the last figures are retained as tending to prevent the accumulation of small errors in the calculations.

The diffusion tubes A and B are composite in character, and each consists of eight tubes of average length 4·874 cms.; the average area of cross-section of each battery is 0·40515 sq. cm.

The capillary tube has an average internal diameter of 1·06 mm., and when calculating the head required to overcome the viscous resistance its length is taken to be 150 cm.

The glass vessels E and F, which may be called traps, because their function is to catch the salt transmitted along A and B, have each a capacity of 1,200 cubic cm.

The tank has a capacity of over 20 litres.

The capillary tube is provided with two main taps, G and H. The new arrangement for introducing the coloured index is suggested by I. (For the old method see Fig. 3, p. 196, "Proc." Phys. Soc., Vol. XXIII., Part III., 1911.) J is a vertical tube at right angles to the capillary. Tubes PQ and RS enable the traps to be filled and emptied. All taps and ends of tubes are provided with seals of liquid, generally mercury. The figure is diagrammatic, and in reality the two halves of the capillary tube are in the same horizontal plane.

§ 4. *Method of Conducting the Experiment.*

Distilled water to which a trace of copper chloride has been added was placed in aspirators and the dissolved air removed by connecting the aspirator to an exhaust pump. The copper chloride is added to kill or retard fungoid growths. Air-free water has two advantages :—

(*a*) Any small air bubble that has not been removed from the apparatus is speedily dissolved.

(*b*) Fungoid growths do not develop in freshly evacuated water—at any rate, in the author's experience.

After being stirred in a large carboy the water is added to the tank T and to the traps F and E. In order to prevent strain in the process of filling, care is taken to keep the levels of the water in F, E and T approximately the same. An exhaust pump is then attached to J and the whole apparatus filled with water. The apparatus is left to stand for a day or two. The main taps G and H are then closed and the tank is slowly filled with an evacuated solution of potassium chloride, to which a trace of copper chloride has been added.

The taps G and H are then opened, and after some days a coloured index is introduced into the circuit. The index liquid consists of an aqueous solution of uranine (generally ¼ gramme to the litre), to which a trace of copper chloride has been added. One cubic centimetre of a 20 per cent. solution of copper chloride was, as a rule, added to 20 litres of all the liquids employed.

§ 5. *References to Discarded Forms of Apparatus.*

Altogether about a dozen pieces of apparatus have been employed. Some of the devices were discarded in the attempt to avoid the mysterious disturbances, others were given up because of difficulties of construction. In one form of the apparatus the tank was small, and the four short tubes leading to the traps F and E passed through the base of the tank. One of each pair of tubes proceeded to the bottom of the trap concerned. Each tube was provided with a three-way tap, so that it was possible to replenish the traps with pure water. It was hoped to analyse the liquid from the traps and to confirm the value of k found by the flow. In another form of the apparatus there was a device involving the use of a mercury seal, which enabled that part of the apparatus which holds the diffusion tube A to be adjusted by means of three screws.

Calculations of Results and Notes on Experiments.

It may be noted that, in the calculations to a first approximation, it is unnecessary to know the values of b, N and z, and that in calculations of precision it is unnecessary to know them with any extreme accuracy. Throughout the experiments b has been taken as 0·4058 and z as 0·000607 cm. of water. N was varied with the experiment.

§ 6. *Specimen Results with the Discarded Reservoir Method of Introducing Index.*

1. N=0·192 gramme per cubic centimetre, h=0·763 cm. The index was introduced 14 days after the filling of the apparatus. The first reading was taken a day later. In the table shown below the first column gives the hours elapsed after the first reading of the index, the second column gives the reading of the index, the third gives the speed of the index in the interval in centimetres per hour, the fourth gives the average speed after the first reading, the fifth gives the temperature in the interval.

Time in hours.	Reading in cms.	Speed in interval.	Speed from start.	Temperature in interval.
0	5·7	...	...	...
24·08	16·59	0·450	0·450	19·15°C.
48·08	27·78	0·466	0·458	19·05°C.
96·11	50·66	0·476	0·467	19·05°C.
168·08	85·55	0·485	0·475	19·09°C.
192·11	96·94	0·474	0·475	19·13°C.
216·08	108·61	0·487	0·476	19·14°C.
264·16	131·43	0·475	0·476	19·10°C.

A graph gives a convincing proof that there was a non-erratic action at work during the series of observations.

The speed at the end deduced from the tangent to the graph was 0·478 cm. per hour.

The temperature may be taken at 19·1°C.

The value of k obtained by means of (13), (14), (15) and (16) and (12) is $1{\cdot}552\times10^{-5}$, and by means of (17), (18) and (19) it is $1{\cdot}550\times10^{5-}$, and by means of (20) it is $1{\cdot}552\times10^{-5}$.

A second index was introduced. The speed on the second day after the introduction of the index was 0·18 cm. per hour—*i.e.*, less than half what it would have been if no disturbance had been caused in the process of introducing the new index.

On the third day the speed was 0·44 cm. per hour, and it increased to 0·46 in the course of the following week.

2. $N=0{\cdot}203$ grammes per cubic centimetre. $h=0{\cdot}821$ cm.

The speed was between the limits 0·43 cm. and 0·54 cm. per hour.

If the hypothesis be made that the disturbance is statical and not dynamical in character, then the best value of the speed is the highest—viz., 0·54 cm. per hour. The temperature may be taken as 18·9°C., the value of k from (12), &c., is $1{\cdot}628\times10^{-5}$, from (17), &c., it is $1{\cdot}629\times10^{-5}$, from (20) it is $1{\cdot}629\times10^{-5}$. *This result agrees to 2 per cent. with the value given with the superior method of introducing the index.*

§ 7. *Experiments and Results with the Successful Tap Plug Method of Introducing Index.*

By introducing a second index whilst a first was in the middle of its journey it was proved conclusively that the introduction of the index does not produce a large disturbance. The readings suggest that in general the introduction of a second index increases the reading of the first index by 1 mm. The effect may be due to mechanical disturbance in the process of introducing the second index. The tap, made abroad, was not according to specification, and the index was long and diffuse and not symmetrical. Readings were made of the two ends and the average taken. Mrs. Griffiths, Mr. H. G. Bell and the author took independent readings of an index, and the calculated speeds during one experiment were 0·537, 0·537 and 0·540 respectively, so that, in spite of the poor index, the results were consistent. After the improved method of reading a bad index, described in a following Paper, had been evolved, it was proved that the earlier method of taking the reading gives substantially accurate results.

An attempt was made to determine *k* for weak solutions; but, unfortunately, various deposits had formed and adhered to the glass in various parts of the interior of the apparatus; and as, on account of the cements employed in putting the apparatus together, an attempt to clean the interior only made matters worse, the instrument had to be dismantled.

The variety and manner in which growths form in the apparatus is annoying and remarkable. A white growth frequently formed in the vertical tube J. An expert chemist thought the growth was botanical, whilst an expert botanist thought it was chemical. A white curdy deposit often formed near a tap even when no lubricant was used. Over long periods the use of a copper salt for keeping down fungoid growths is not very satisfactory. The salt appears gradually to come out of solution, perhaps as an oxy-salt; at any rate, living fungoid growths do sometimes appear in the solution after some weeks.

The results given by experiments in which the conditions were kept constant throughout the long series of observations are set out in the following table. ${}_0K_N$ is given in C.G.S. units.

	Diff. of level.	Speed in cms. per hour.	*v*.	N.	Temp.	${}_0K_N$.
1	0·788	0·535	$3{\cdot}244\times10^{-6}$	0·213	20·0	$1{\cdot}691\times10^{-5}$
2	0·788	0·542	$3{\cdot}286\times10^{-6}$	0·213	20·2	$1{\cdot}710\times10^{-5}$
3	0·788	0·539	$3{\cdot}268\times10^{-6}$	0·213	20·3	$1{\cdot}700\times10^{-5}$
4	0·788	0·538	$3{\cdot}262\times10^{-6}$	0·210	20·2	$1{\cdot}696\times10^{-5}$

The results of the above table give a mean value of ${}_0K_N$, equal to $1{\cdot}70\times10^{-5}$ at a temperature of 20·2°C. in the case of an aqueous solution of potassium chloride containing 0·21 grammes of salt to the cubic centimetre. This is 6 per cent. higher than that obtained by the author's colleague, Mr. B. W. Clack. The difference is small compared with the differences between the published results in diffusion; but it is probably just outside the errors of observation and further research is necessary.

In conclusion, the author would like to express his indebtedness to Mr. W. E. Paterson, M.A., B.Sc., Rev. M. Collett, B.Sc., Mr. J. M. Dickson, B.Sc., Mr. M. C. Boff, Mr. H. G. Bell and Mrs. C. H. Griffiths, B.Sc., for much painstaking help in very monotonous tasks.

N.B.—In a previous Paper by the author, "Proc." Phys. Soc., XVI., Part IV., pp. 230–243, the following errors occur :

Page 235 *line* 23, 5·09 *should be* 0·727
" 238 " 14, 5 " 0·7
" 242 " 12, 0·019 " 0·19
" 242 " 13, 0·08 " 0·8

ABSTRACT.

In general the diffusion of matter like the diffusion of heat produces convective currents, and there is a diffusive convection which is akin to thermal convection. In the apparatus described in the Paper the convective flow is of the order of one millionth of a cubic centimetre per second from the top of one set of diffusion tubes to the top of another set. The top of each set of diffusion tubes is enclosed in a glass vessel containing water, and the one vessel is connected to the other by means of a long capillary tube. Each set of eight diffusion tubes is of length about 5 cm., and has a total area of cross-section of about 0·5 sq. cm. The capillary tube is about 150 cm. long, and has a diameter of about 1 mm. ; and the linear flow of a coloured index, consisting of a feeble solution of uranine, is of the order of 10 cm. per day. The index is introduced by means of a special four-way glass tap.

DISCUSSION.

Mr. B. W. CLACK said he had repeated his experiments under all possible conditions to try to locate the cause of the 6 per cent. difference between his results and those of the author, but so far without success. In the author's arrangement the water was inside the tube and the solution was in the tank. He had tried that with his apparatus but gave it up in 1908 in favour of having the water in the tank and the solution inside. He showed some curves taken with the two arrangements. In the case of dilute solutions the results were the same, but with strong solutions there was about 4 per cent. difference. It may be in this direction that the explanation of the discrepancy has to be looked for.

Dr. T. BARRATT asked if the introduction of a salt to prevent the formation of fungoid growths would not be likely to cause some error.

Dr. GRIFFITHS replied that the amount of copper chloride introduced was exceedingly small, about 1 cubic cm. of 20 per cent. solution being added to the liquid in question, and he did not think it could produce any appreciable error.

IV. *The Effect of Electric Oscillations on the Magnetic Properties of Iron investigated by the Campograph. By* J. A. FLEMING, *M.A., D.Sc., F.R.S., and* P. R. COURSEY, *B.Sc.*

RECEIVED OCTOBER 25, 1915.

IN a Paper read to the Physical Society in March, 1915, by one of us (Dr. J. A. Fleming), a description was given of an instrument invented by him for delineating physical curves which he called a campograph.* Since that date great improvements have been made by him in the instrument by the substitution of mirrors of worked glass silvered on the front for the common silvered-on-the-back mirrors first employed which has resulted in a great optical improvement and in a resulting fineness in the lines on the photographic plates. The object of the following research was to apply this improved instrument in the study of the effects on the hysteresis curves of iron of superimposed oscillations or currents through the iron. For the arrangements adopted we refer to the Paper of Dr. Fleming (*loc. cit.*). Suffice it to say that a new magnetising helix of 71,136 turns was constructed 1 metre in length and the iron wires employed were of 50 cm. in length and about 2 mm. in diameter. Hence the iron may be regarded as placed in a nearly uniform field. We refer also to the above-mentioned Paper for details as to the mode of calibration of the campograph so as to determine the absolute value of the hysteresis from the photographic delineation of the curves.

The iron wire employed was placed in this long magnetising helix and fixed in position near the magnetometer and campograph. It was then easy to photograph a hysteresis loop for the iron by slowly varying in a cyclical manner a direct current through the magnetising helix. The illustrations in this paper are reproduced from the actual negatives, each taken in a very few minutes. Also at the same time alternating currents or high-frequency oscillations could be passed through the iron wire, or made to circulate round it, through an inner helix wound on the iron wire. This last coil had 800 turns of No. 26 S.W.G. copper wire, and the length of the helix was 46·5 cm. The R.M.S. value of the electric oscillations damped or undamped which passed through it was measured by a thermo-electric ammeter.

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* "An Instrument for the Optical Delineation and Projection of Physical Curves," by J. A. Fleming, "Proc." Phys. Soc. Lond., Vol. XXVII., p. 316, 1915.

These dispositions being made we proceeded to study the effect on the magnetic hysteresis of iron of electric oscillations flowing around the wire or else along it, whilst at the same time the iron was subjected to a slowly varying cyclical magnetising force under various conditions.

1. The first group of observations were on the effect of damped electric oscillations of constant R.M.S. value (about 70 milliamperes) and constant oscillation frequency (about $0 \cdot 75 \times 10^6$), and spark frequency (about 250), but the maximum value of the slow cyclical magnetising force varying from about $H_{max.} = 1$ to $H_{max.} = 10$. This effect is different for small forces and large. If $H_{max.}$ lies between about 0·2 and 3 C.G.S. the effect of the oscillations is to produce a very marked increase in the hysteresis and a marked increase in the magnetic flux corresponding to the maximum force, with a maximum effect in the neighbourhood of $H = 0 \cdot 5$ to $0 \cdot 7$. If $H_{max.}$ lies between 3 and 6 then the effect is in the same direction but less marked. If, however, $H_{max.}$ is about 8 or 10 then the hysteresis loop becomes smaller by the corners being rounded off. These various effects are shown by the photographs in Fig. 1, 2 and 3. Hence, for small slowly cyclical magnetising forces the effect of superimposing electric oscillations is greatly to increase the hysteresis loss and also the magnetic flux density corresponding to the maximum force. For large maximum cyclical forces the effect of the oscillations is to diminish the flux at or near the zero value of the magnetising force. Since the coil carrying the oscillations had 800 turns and a length of 46·5 cm. it will be seen that the turns per centimetre are 17·2, and hence the magnetising force for 70 milliamperes is $H = 1 \cdot 5$.

For the damped oscillations used in this set of experiments the ratio of the maximum value of the current in a train to the R.M.S. value was very nearly 100. Hence the magnetising force rose at some instants to nearly 150, but had an R.M.S. value of 1·5. It follows, therefore, that the oscillatory magnetic force carried up the flux density to saturation at certain instants 250 times a second. The explanation of the above effects may be as follows: Superimposed upon the slowly cyclical force we have a rapidly cyclical force of very varying maximum. The effect of this is to shake up the magnetic molecules of the iron and to promote greater responsive magnetisation to the slow cyclical force at the extreme ends of the cycle, but this action also increases the retentivity and, therefore, the hysteresis. On the other hand, for large values of

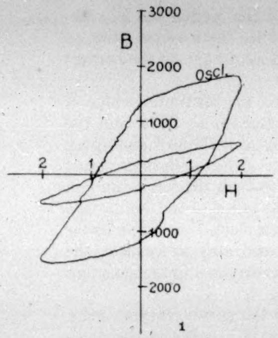

FIG 1.

R.M.S. current=70 × 10^{-3}amp.; frequency=0·75 × 10^6; spark frequency=250 per second; decrement=0·68.

Hysteresis loss per cm.^{3} per cycle: normal =117 ergs; with oscillations=482 ergs.

Maximum flux density=600 (normal), with oscillations=1,730.

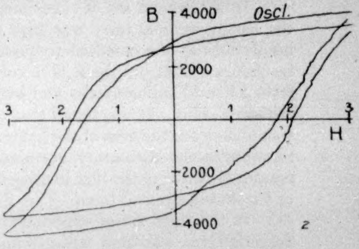

FIG. 2.

Current=70 × 10^{-3}amp.; frequency=0·75 × 10^6 spark frequency=250 per second; decrement =0·68.

Hysteresis loss per cm.^{3} per cycle: normal =1,800 ergs; with oscillations=1,810 ergs.

Maximum flux density: normal =3,470; with oscillations=4,190.

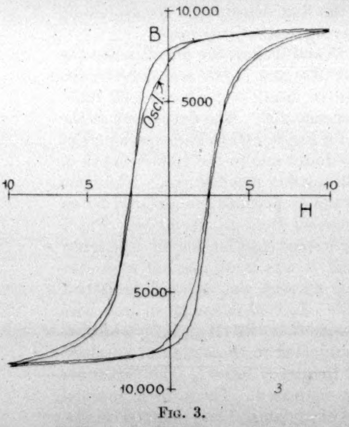

FIG. 3.

R.M.S. current=70 × 10^{-3} amp.; frequency =0·75 × 10^6; spark frequency=250 per second; decrement=0·68.

Hysteresis loss per cm.^{3} per cycle: normal =7,360 ergs; with oscillations=6,770 ergs.

Maximum flux density: normal=8,820; with oscillations=8,900.

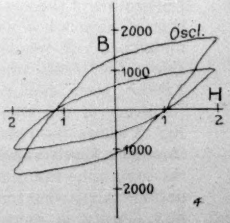

FIG. 4.

R.M.S. current=57 × 10^{-3} amp.; frequency =0·75 × 10^6; spark frequency=250 per second decrement=0·68.

Hysteresis loss per cm.^{3} per cycle: normal =250 ergs; with oscillations=490 ergs.

Maximum flux density: normal=840; with oscillations=1,450.

the slowly periodic force the effect of the oscillations is somewhat to reduce retentivity and so reduce the magnetisation at the moments of zero force and, therefore, to cut off the corners of the hysteresis loop.

2. In the second set of experiments the maximum value of the slowly cyclical force was kept constant at $H=2$ and the oscillations at the constant frequency of $0{\cdot}75\times 10^6$ and spark frequency at 250, but the R.M.S. value of the oscillations varied from 23 to 57 milliamperes, and hence their magnetic force in the same ratio. It was found that the effect of the oscillations was to increase the area of the hysteresis loop almost in a linear relation to the oscillatory currents and also to increase the maximum value of the flux density corresponding to maximum of the slowly cyclical force. (*See* Fig. 4.)

3. In the third set of experiments the slowly varying magnetising force was kept within limits $H_{max.}=2$ and the oscillatory current kept of constant R.M.S. value (60 milliamperes), but its oscillation frequency varied from $0{\cdot}75\times 10^6$ downwards. The spark frequency was kept at 250 for the high-frequency damped oscillations. In this case there was a very marked increase in both the area of the hysteresis curve and in the maximum value of the flux density (B) corresponding to the maximum slowly varying magnetising force.

The photographs in Figs. 5 and 6 show the effects when the oscillation frequency was 100,000 and 11,000 respectively, the R.M.S. value of the oscillations being in both cases 60 milliamperes and the spark frequency 250. The decrement in the case of Fig. 5 was 0·265 and for Fig. 6, 1·07. The superior effect of the lower frequency is no doubt due to the greater depth of penetration of the low-frequency flux into the iron. The same type of effect takes place if the oscillations are replaced by an undamped high-frequency current from an alternator. Fig. 7 shows the result when persistent oscillations of frequency 2,800∼ were employed, and it was most marked when the frequency of the alternating current was reduced to 100∼. Fig. 8 shows the remarkable effect of carrying an iron wire through a slowly varying magnetic cycle ($H_{max.}=2$), whilst at the same time the iron is subjected to the action of an alternating magnetising force of frequency 100∼. The maximum flux density is immensely increased. There is a marked difference between the effect of undamped and damped oscillations of the same R.M.S. value and frequency. Thus Fig. 9 shows the result of superposing an alternating current of 45

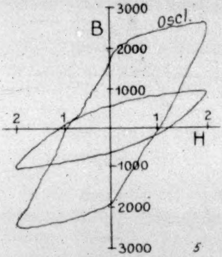

Fig. 5.

R.M.S. current $=60\times10^{-3}$ amp.; frequency $=10^5$; spark frequency $=250$ per second; decrement $=0{\cdot}26$.

Hysteresis loss per cm.^{3} per cycle: normal $=262$ ergs; with oscillations $=675$ ergs.

Maximum flux density: normal $=945$; with oscillations $=2{,}520$.

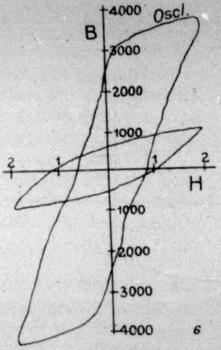

Fig. 6.

R.M.S. current $=60\times10^{-3}$ amp.; frequency $=11{,}000$ spark frequency $=250$; decrement $=1{\cdot}07$.

Hysteresis loss per cm.^{3} per cycle: normal $=231$ ergs; with oscillations $=885$ ergs.

Maximum flux density: normal $=960$; with oscillations $=4{,}050$.

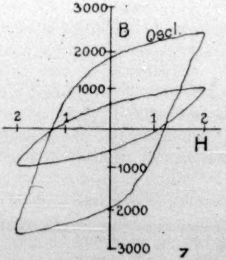

Fig. 7.

R.M.S. current $=60\times10^{-3}$ amp.; frequency $=2{,}800$; decrement $=0$.

Hysteresis loss per cm.^{3} per cycle: normal $=263$ ergs; with oscillations $=760$ ergs.

Maximum flux density: normal $=965$; with oscillations $=2{,}480$.

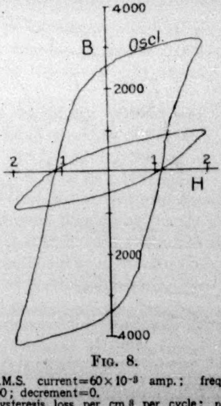

Fig. 8.

R.M.S. current $=60\times10^{-3}$ amp.; frequency $=100$; decrement $=0$.

Hysteresis loss per cm.^{3} per cycle: normal $=239$ ergs; with oscillations $=1{,}150$ ergs.

Maximum flux density: normal $=930$; with oscillations $=3{,}720$.

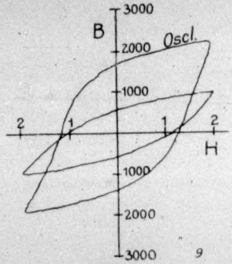

FIG. 9.

R.M.S. current=45×10^{-8} amp.; frequency =4,500; decrement=0.

Hysteresis loss per cm.^{3} per cycle: normal=256 ergs; with oscillations=655 ergs.

Maximum flux density: normal=972; with oscillations=2,050.

Compare with Fig. 10.

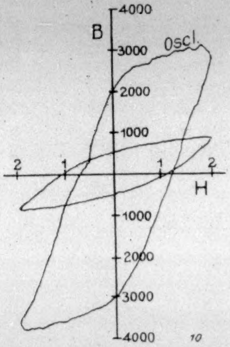

FIG. 10.

R.M.S. current=45×10^{-8} amp.; frequency =4,500; spark frequency=250 per second; decrement=0·51.

Hysteresis loss per cm.^{3} per cycle: normal =228 ergs; with oscillations=912 ergs.

Maximum flux density: normal=905; with oscillations=3,420.

Compare with Fig. 9.

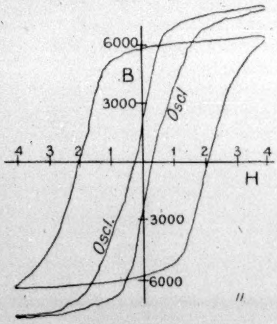

FIG. 11.

R.M.S. current=9·5 amps. along the wire; frequency=186,000; spark frequency=200; decrement=0·209.

Hysteresis loss in ergs per cm.^{3} per cycle: normal =4,110; with oscillations=1,010.

Maximum flux density: normal=6,320 with oscillations=7,900.

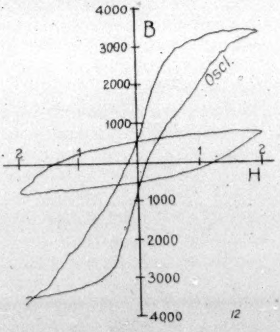

FIG. 12.

R.M.S. current=9·5 amps. along the wire; frequency=186,000; decrement=0·209; spark frequency=abt. 200.

Hysteresis loss in ergs per cm.^{3} per cycle: normal =250; with oscillations=282.

Maximum flux density: normal=778; with oscillations=3,460.

milliamperes and frequency 4,500 on a slowly varying magnetic cycle, whilst Fig. 10 shows the effect of using a damped oscillation of decrement 0·51, but the same frequency and R.M.S. value. The increase in maximum flux density produced by the damped oscillations is greater than by the undamped. Since in the latter case the ratio of maximum to R.M.S. value is much greater, this seems to indicate that the maximum value of the force is effective.

4. In the fourth set of experiments the effect of sending damped or undamped oscillations of various strengths and frequencies along an iron wire, on the magnetic hysteresis curve due to slowly varying force was investigated.

In the first place the oscillations used were damped oscillations of R.M.S. value 0·58 ampere, frequency $0{\cdot}488 \times 10^6$ and decrement 0·172. The maximum value of the slowly cyclical magnetising force varied from $H_{\text{max.}} = 2$ to $H_{\text{max.}} = 10$ in different experiments.

The effect was found to be generally much the same as when the oscillations passed round the wire, viz., for small maximum value of H the hysteresis loop was increased and for values of $H_{\text{max.}} = 8$ or 10 the area was diminished by the shoulders of the curve being rounded off.

In the second set of experiments an oscillatory current of 9·5 amperes was used, and the frequency lowered to 186,000 and decrement was 0·209. The spark frequency was about 200.

In a third set of experiments the oscillatory current was carried up to 20 amperes, at an oscillation frequency of 477,000 and decrement of 0·156. When the slowly varying magnetic force had a maximum value of about 3 to 4 or more the effect of the oscillations in this case was to close up or diminish the area of the hysteresis loop by an amount depending on the current strength, but at the same time it increased the maximum value of the flux density very greatly for small maximum values of the slowly varying cyclical magnetising force. (*See* Figs. 11, 12 and 13.)

There is, therefore, a double action. The hysteresis is diminished, but the magnetisation is increased at the extreme ends of the cyclical curve, except when the current is very large when the extreme magnetisation is diminished. This diminution of the hysteresis is also found when a strong continuous current is sent along the wire. It is not an effect due

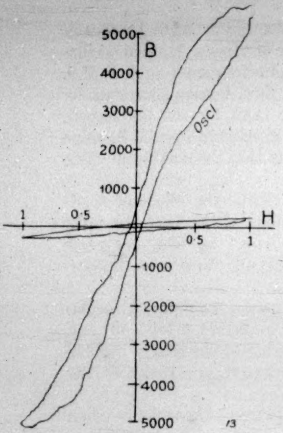

Fig. 13.

R.M.S. current=9·5 amps. along the wire; frequency=186,000; spark frequency=abt. 200; decrement=0·209.

Hysteresis loss per cm.³ per cycle, in ergs: normal =24·3; with oscillations=195.

Maximum flux density: normal=286; with oscillations=5,440.

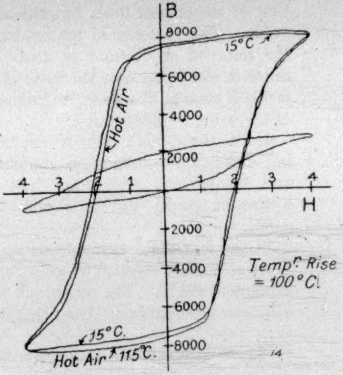

Fig. 14.

Direct current=15 amps. along wire.

Hysteresis loss per cm.³ per cycle: normal =5,160 ergs; with hot air=5,200 ergs; with current=850 ergs.

Maximum flux density: normal=8,150; with hot air=8,150; with current=1,860.

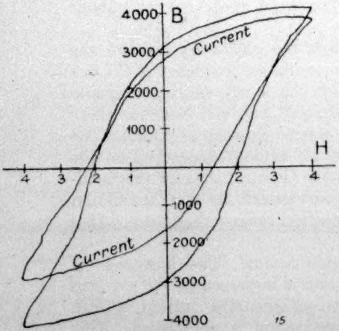

Fig. 15.

Direct current along tube=15 amps.

Hysteresis loss in ergs per cm.³ per cycle: normal =2,285; with current=1,715.

Maximum flux density: normal=4,140; with current=3,360.

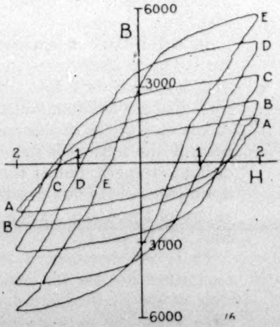

Fig. 16.

Frequency=80 ∽; decrement=0.

Curve.	Current.	Loss in ergs.	B_{max}
A	0	475	1,760
B	0·25	813	2,380
C	0·50	1,190	3,400
D	0·75	1,340	4,580
E	1·0	976	5,640

Current along iron wire.

to heat.* This was proved by sending along the iron wire a current of hot air. In other words, when the wire was heated by hot air to about the same temperature (115°C.) that it was heated by the electric current sent along it, no sensible diminution in area of the hysteresis loop was found. (*See* Fig. 14.)

It is clear, however, that this diminution of the hysteresis, as shown by the smaller loop in Fig. 14, is the result of the strong circular magnetisation produced by the current, whether direct or alternating, flowing along the wire. It is well known that the hysteresis loss of iron is reduced to a small value when the iron is rotated in a very strong magnetic field. If, then, a strong current flows along a rather thin iron wire producing a circular magnetisation, the corresponding circular magnetic flux may reach a high value, and the result of superimposing a slowly cyclical longitudinal magnetisation may be that the hysteresis loss due to the latter is greatly reduced. The magnetic force just at the surface of the iron wire is $A/5r$, where A is the current conveyed in amperes, and r is the radius of the wire in centimetres. In this case $A=15$ nearly and $r=0{\cdot}08$ cm. Hence the force is about 37 C.G.S. units.

There is accordingly a strong circular magnetisation, and this grips the molecules so that it reduces the hysteresis under longitudinal force. Moreover, when the current is very strong it reduces the longitudinal magnetisation. This view was confirmed by using a thin walled tube of iron instead of a solid wire, the total cross-section of iron and the current flowing through it being the same in both cases. The two diagrams in Figs. 14 and 15 show the two cases of a solid iron wire and an equi-sectional iron tube of overall diameter of 1 cm. It is clear that in the case of the tube the circular magnetising force at the surface is much less than in the case of the thin wire for equal current conveyed. Hence we find that in the case of the tube there is a much less reduction in the area of the hysteresis loop due to slowly varying longitudinal force. The above explanation therefore seems valid.

When the longitudinal cyclical force has a small maximum value $H=1$ the effect of sending strong oscillatory currents along the wire is to produce a remarkable increase in the maximum flux density at the extreme ends of the cycle. It also increases the area of the loop, as shown in Fig. 13. The superimposed oscillations then promote magnetisation by shaking up the magnetic molecules both when the electric oscillations flow along the wire and when they flow round it through an insulated helix.

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* In the Paper by Dr. J. A. Fleming describing the campograph, *see* "Proc." Phys. Soc., Lond., June, 1915, in Fig. 8 of that Paper the reduction in area of a hysteresis loop due to the passage of a current along the wire is erroneously attributed to heat, whereas it is, in fact, due to circular magnetisation.

If, then, we send along the wire various oscillatory currents at constant frequency, but at the same time vary the maximum value of the slowly cyclical magnetising force, the result is that the hysteresis loop is increased for small maximum values (H=1) of H, but diminished for larger values (H=4 to 8), but the maximum value of the flux density at the ends of the loop is always increased, except in the case of very large values of $H_{max.}$ and of current, when there is a decrease. The oscillations, therefore, increase the apparent permeability at the maximum magnetisation when $H_{max.}$ is less than 8 but slightly decrease it for larger values.

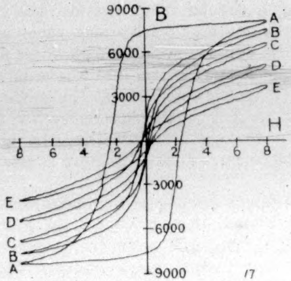

FIG. 17.

Frequency=80 ∽; decrement=0.

Curve.		Current.		Loss in ergs.		$B_{max.}$
A	..	0	..	6,650	..	8,220
B	..	4·5	..	753	..	7,650
C	..	7·0	..	615	..	6,750
D	..	12·0	..	684	..	5,250
E	..	20·0	..	615	..	3,920

Current along iron wire.

5. The effect was next studied of sending a low frequency (n=80∽) alternating current along the wire, whilst at the same time a slowly varying cyclical longitudinal magnetising force was applied to the wire. Out of a large number of photographs two are selected which show the results for $H_{max.}=2$

and $H_{max.}=8$, and for currents varying from 0·25 ampere to 20 amperes. (*See* Figs. 16 and 17.)

In these diagrams the curves marked A are the original hysteresis loops, and the other curves B, C, D, E are the loops when the longitudinal currents of the strength stated below the diagrams flow along the wire. Fig. 16 shows the increase in apparent permeability at the ends of the cycle, and Fig. 17 the reduction both in hysteresis and longitudinal permeability for strong currents due to the circular magnetisation.

6. To extend these results the campograph connections were re-arranged so as to delineate an ordinary magnetisation (non-cyclical) curve. The magnetisation curve was then taken with and without an oscillatory current of 60 milliamperes at a frequency of $0{\cdot}75\times10^6$ and decrement=0·68 flowing round the wire. The result is shown in Fig. 18, by which it is seen that the effect is slightly to increase the flux at two points on the magnetisation curve.

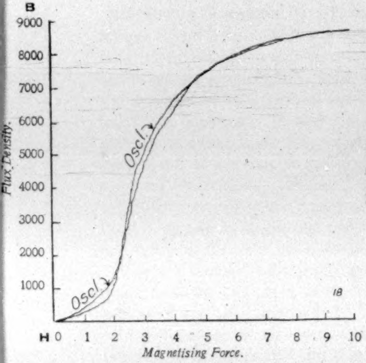

FIG. 18.

R.M.S. current=60×10^{-3} amp.; frequency =$0{\cdot}75\times10^6$; decrement=0·68.
Spark frequency=250 per second.

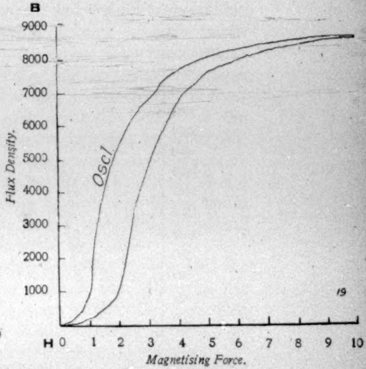

FIG. 19.

R.M.S. current=60×10^{-3} amp.; frequency =100; decrement=0.

In the next case the magnetisation curve was photographed with and without a persistent alternating low-frequency current ($n=100$) of 60 milliamperes flowing round the wire. The effect is shown in Fig. 19, and is seen to be a great increase in flux density all along the curve. For magnetising forces near H=2 the flux density is increased about five times, as shown in Fig. 20, which gives the permeability curves deduced from Figs. 18 and 19.

Conclusions.—The photographs reproduced in this Paper are only a few out of a very large number taken, which have all been carefully analysed. Broadly and generally, the effect on an iron wire of a longitudinal slowly varying cyclical magnetising force, on which an alternating magnetisation, also longitudinal or else circular, is superimposed, is as follows: When the cyclical magnetic force has a small maximum ($H=1$ about) the effect either of superimposed damped or undamped oscillations of high or low frequency is to increase the hysteresis loss and to promote or increase the magnetisation at the extreme ends of the cycle. If. however, the cyclical force has a larger maximum ($H=8$ or more) then the general result is to diminish the hysteres is loss. Except in the case of strong currents (10 to 20 amperes) sent along the wire the general effect of either longitudinal or circular alternating magnetising force, damped or undamped, is to increase the magnetisation at the ends of the cycle; in other words, to increase the apparent permeability corresponding to the maximum magnetising forces. The oscillations or alternating currents, which, though taken alone, have relatively a small (R.M.S.) magnetising force,

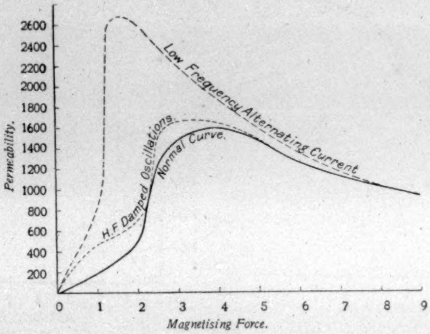

FIG. 20.

Effect of oscillatory fields on the permeability of iron wire.
L.F. current$=60\times10^{-8}$ amp. at 100 ∽. H.F. current$=60\times10^{-8}$ amp. at $0{\cdot}75\times10^{6}$ ∽ and decrement$=0{\cdot}68$.

appear to shake up the iron and so promote the magnetisation by the slowly periodic longitudinal magnetising forces.

Experiment shows that mechanical shocks or vibrations act very much in the same manner. If an iron wire is placed in a helix and a weak magnetising force $H < 1$ applied, then small twists or tapping the wire greatly increases the resultant magnetisation. If the magnetising force is removed and the twisting or mechanical shock subsequently applied then the remanent magnetisation is reduced.

In all cases it is found that the increase of hysteresis loss, and of apparent permeability at the extreme end of a cycle of magnetising force, reaches a maximum value for some particular strength of current through the wire. The value of this optimum current (R.M.S. value) depends upon the maximum value of the slowly cyclical force, being greater for small than for large maxima. It also depends upon the nature of the current whether high or low frequency, damped or undamped. In general it appears to be much greater for high-frequency damped oscillations. Hence it is probable that if very strong oscillatory currents were sent along an iron wire there would be a decrease in hysteresis under slowly periodic longitudinal magnetising forces of even small maximum value.

There is clearly a diminishing action on the hysteresis if the current along the wire is strong enough, but otherwise the action of the oscillations is to increase hysteresis. The joint effect is, therefore, the resultant of two opposing actions, one tending to increase and the other to diminish hysteresis.

It would occupy far too much space to make even a brief reference to the extensive previous work done on the subject of the effect of electric oscillations on the magnetic hysteresis and permeability of iron and steel. The investigations of Dr. W. H. Eccles, Dr. J. Russell, Mr. L. H. Walter, M. C. Mauvain, and also the contributions of Ascoli, Arno, Piola and P. Duhem on this subject are well known. We think it will be found that the above photographs taken with the campograph are not inconsistent with, but generally confirm, the conclusions of the above-named investigators. One thing is certain, viz., that the result of electric oscillations on iron superimposed on a slowly cyclical magnetic force is not always to diminish or to increase the hysteresis loss, but the results are dependent upon a number of factors and cannot be embodied in any short statement. The effects greatly depend upon the relative value of the maximum magnetising forces which are imposed on the ron, one the slowly cyclical, and the other the rapidly varying one.

A result of considerable interest and perhaps of practical value is the proof given above that the passage of a strong unvarying or else alternating current through an iron wire immensely decreases the hysteresis due to a superimposed slowly varying longitudinal magnetic force, and that in some cases this may result also in a very considerable increase in the apparent permeability of the iron to this longitudinal force. The above results carry with them an explanation of the action of magnetic detectors of all kinds in wireless telegraphy, but it would occupy too much space to enter into the discussion of them.

ABSTRACT.

At a meeting of the Society in March, 1915, Dr. J. A. Fleming exhibited an instrument which he called a campograph, for photographing and delineating physical curves. Since then the optical arrangements have been greatly improved, and the point of light travelling over the photographic plate is now extremely small and sharp. With this improved campograph the authors have investigated the effect of electric oscillations on the hysteresis and permeability of iron. The general results are as follows :—

1. When an iron wire is taken slowly through a magnetic cycle and a superposed high-frequency magnetising force is also applied, then, if the maximum value of the slowly periodic longitudinal magnetic force does not exceed a certain value, the effect of the oscillations is to increase the area of the hysteresis loop and to increase the magnetisation at the ends of the cycle.

2. If the slowly periodic force has a large maximum value then the hysteresis loop is diminished in area, but the maximum magnetisation remains unaltered.

3. The increase in area of the hysteresis loop is generally less for high frequency than for low frequency oscillations, because in the latter case the oscillatory flux penetrates further into the iron wire.

4. If oscillatory currents are passed along the iron wire whilst at the same time the iron is taken slowly through a longitudinal magnetic cycle with continuous current, then when the oscillatory current has a small R.M.S. value the effects are generally similar to those produced by longitudinal oscillatory magnetic forces. If the oscillatory current is relatively large then their effect is to reduce the hysteresis and magnetisation at the ends of the cycle. This last action is due to the circular magnetisation produced by the longitudinal current, which grips the magnetic molecules of the iron, and prevents their longitudinal colineation and reduces also the hysteresis.

The same effect is seen when a longitudinal continuous current is passed along an iron wire.

5. The effect of superimposing on a steady feeble longitudinal magnetic force an alternating magnetic force either by undamped or

damped oscillations is greatly to increase the permeability at the ends of the cycle, provided the oscillatory force does not exceed a certain value. Beyond that a diminution sets in.

Photographs of the various effects were shown.

DISCUSSION.

Prof. **Howe** thought the Paper was a valuable addition to the knowledge of the effects of oscillatory fields on the magnetisation of iron.

Mr. D. **Owen** thought the rapidity with which investigations could be made with the instrument was very helpful. One would expect that the effect of a strong current passed along an iron wire which was magnetised longitudinally would be to remove the longitudinal magnetisation completely. This, however, was not the case. In some experiments he had once performed on the effect of currents along the wire superposed on a longitudinally magnetising force it appeared to be immaterial whether the currents were alternating or direct.

Lieut.-Col. **Squier** admired the instrument. The results would, he thought, repay careful study.

Dr. C. **Chree** was reminded by many of the results described of the combined effects of mechanical stresses and magnetic forces. Mechanical oscillations produce many similar effects, and he thought it possible that some of the observed phenomena were due to such mechanical oscillations being set up by the alternating magnetic forces.

Dr. S. W. J. **Smith** also thought that the results were mainly due to mechanical oscillations set up by the varying fields. Considerable work had been done on the subject. He quoted several observers who had described very similar phenomena produced by mechanical treatment, and indicated how oscillation of the molecular magnets gave rise to several of the effects.

Prof. **Fleming**, replying for the authors, said that it had only been possible to give a very rapid sketch of the phenomena. Many observers had worked on the subject, and he did not think any of the results described in the Paper were antagonistic to those already accepted. The principal point of the present Paper was, however, to indicate the rapidity and ease with which such experiments could be made by means of the campograph.

V. *A Hydraulic Analogy of the Wheatstone Bridge, by* MR. R. S. WHIPPLE.

DEMONSTRATION AT THE MEETING OF NOVEMBER 12, 1915.

THE analogy of the flow of water along pipes is frequently used when teaching Ohm's law, but the author does not know of a published description of a simple model. About 18 years ago Prof. H. L. Callendar showed a model of a pneumatic Wheatstone bridge in which the arms of the bridge consisted of small capillary tubes, through which a stream of gas or air could be passed. The galvanometer, or differential pressure indicator, as it was in this case, consisted of a mica vane pivoted in such a manner that it was deflected whenever the pneumatic pressure became greater on one side of the vane than on the other. By means of taps and tubes of various lengths, Prof. Callendar was able to show the effect of increasing or diminishing the length of pipe through which the gas passed.

The objection to the pneumatic model from the teacher's point of view is that the pressure indicator is difficult to make, and that all the taps require good workmanship. In the model shown, glass and indiarubber tubing with some glass taps are all that is required. The solution used is water coloured with ink, and this is allowed to flow slowly through the bridge circuit.

The galvanometer or detector is simply a large air bubble in a horizontal glass tube placed across the bridge arms. A tap is placed in the tube for adjusting the size of the bubble. When the capillary resistance of the tubing on each side of the bridge is equal, the bubble is stationary in the centre of the tube. As soon as the balance of the bridge is disturbed by either partially closing a tap or by introducing another length of tubing by the opening of a tap, the want of balance is shown immediately by the movement of the air bubble. Balance is restored by introducing or diminishing the resistance in the opposite arm of the bridge, and the bubble at once takes up its null position.

VI. *Experiments with Filaments Heated Electrically in Volatile Liquids.* *By* S. W. J. SMITH, *Hon. Sec. Physical Society.*

RECEIVED SEPTEMBER 24, 1915. READ MAY 22, 1914.

1. I was led to perform these experiments by a statement made to me by Mr. C. W. S. Crawley* to the effect that, when a 100 volt lamp filled with paraffin oil is used as a resistance in a 200 volt circuit, the bubbles of gas which form on the filament, instead of rising at once, run down the legs of the filament before they escape to the surface of the liquid.

Attempting to reproduce this phenomenon, I found that if the voltage applied to the lamp were reduced below 100, so that no bubbles formed, it was possible (by momentarily increasing the voltage) to obtain a single bubble upon the wire.

The behaviour of this bubble was most fascinating to watch, and seemed even more mysterious than the observation to which my attention had been drawn.

The bubble ran backwards and forwards from one terminal to the other, "looping the loops" of the filament many times before escaping from the wire!

2. Many other liquids, besides paraffin oil, yield the same result. Benzene, turpentine and aniline may be mentioned as examples.

The currents necessary for the production of the bubble and for its maintenance are higher, the higher the boiling point of the liquid. This suggests that the bubble consists of vapour of the liquid, and the inference is, in fact, usually correct except during the first heatings soon after the liquid is poured into the lamp. Then there will be a certain amount of entrapped air which may provide the nuclei of the earlier bubbles. Indeed, if a very viscous liquid of high boiling point (such as machine oil) is used it is possible by means of a fine pipette to project a minute bubble of air upon the heated wire. This bubble then moves in the same manner as those formed spontaneously.*

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* NOTE BY MR. CRAWLEY.—"The effect in question was shown to me by Mr. Addenbrooke, who was, however, too much occupied to bring it forward himself. The 'pip' of an ordinary incandescent lamp had been broken off and the bulb filled with paraffin oil, for use as a resistance. It was found most satisfactory both as being able to absorb more power than with a vacuum and also to stand momentary overload much better, and for this reason alone it is worth mentioning.

"When the current is flowing there is naturally a strong current of hot oil up the legs of the filament. When sufficient current is used bubbles form on the filament, but these, instead of rising to the surface, run down the legs against both gravity and the upward current of hot oil and come off at the bottom. Having no facilities for investigating the phenomenon, I thought it might be worth while to draw attention to it in the hope that some member of the Society might be tempted to study it. Meanwhile, Dr. Smith has kindly looked into it and carried the matter further and, it seems to me, given the true explanation."—May 27, 1914.

3. Under favourable circumstances, with turpentine for example, it is easy to adjust the current so that a fairly large bubble circulates to and fro for a long time (a quarter of an hour, for instance) without appreciable change in size. Reducing the current a similar steady state can be reached with a bubble of reduced size. If the current be reduced below a certain limit, however, the bubble disappears.

These facts suggest that the contents of the bubble are continually changing, the constant size under any particular gradient being the result of a balance between the increase due to evaporation into the bubble and decrease due to condensation from it.

4. For, assuming as a rough approximation that the bubble is spherical, consider the effect of supposing its temperature to be uniform. The excess pressure within it will be given by $pr=2\sigma$, where r is the radius and σ is the surface tension, at temperature θ, of the bubble. Since p falls and σ rises when the temperature is lowered, it follows that the equilibrium value of r would be increased by lowering θ. But the bubble actually becomes smaller when the temperature is reduced. We must, therefore, conclude that its temperature is not uniform. The gradient from the wire must be such that, although the hottest part of the smaller bubble is colder than that of the larger one, its mean temperature is above that of the larger one.

For a restricted range it is possible that when the temperature of the wire is reduced the mean temperature of the diminishing bubble may rise ; but so soon as this becomes impossible the bubble must collapse, as experience shows.

It will also be noted that a spherical bubble of uniform temperature would be unstable under the conditions of the experiment.

To sum up, it appears from a variety of considerations that the bubble exists in a region of which the temperature changes rapidly in the direction perpendicular to the wire.

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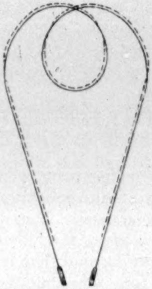
* I have to thank my colleague, Mr. H. Moss, M.Sc., for kindly undertaking to perform this experiment.

5. At first sight it seems possible that the movements of the bubble are due to electrical forces ; but, except that these may play some part in causing the bubble to cling to the wire, it is unlikely that they are appreciable.

The motion of the bubble is not affected by altering the direction of the current. It is produced equally well by alternating currents. It is thus apparently of thermal origin, and seems to be determined only by the temperatures to which the current is capable of raising the wire and its environment.



For convenience, the attempt to explain what is observed may be divided into two parts. Thus we may inquire why a moving bubble should follow the curvature of the wire before attempting to fix the cause of its motion.

6. A reason why a small rising bubble should follow the bend of the filament is not far to seek.

Keeping the current as low as possible, so that the motion of the bubble is comparatively slow and the convection currents from the heated wire are not very pronounced, it is possible to observe fairly easily the track which the bubble follows.* This track is represented by the dotted curves in the figure, the continuous curves denoting the filament of the lamp. The bubble may be said to pass along the "upper" side of each element of the filament. In other words, it runs along the region in which the convection of heated liquid from the filament is a minimum. It is easy to see how such a region arises—permitting a layer of relatively hot liquid to remain in contact with the wire. This " sheltered " layer will be hottest and therefore least viscous nearest the wire. The rate of increase of viscosity outwards will be greatest in a liquid for which the conductivity is small and the temperature coefficient of viscosity large. The bubble, moving along the wire, will be moving in a region in which the viscous resistance to the motion of that half of it which is nearer the wire is less than that experienced by the more distant half. Hence the bubble will be subject to a force tending to press it towards the wire, and this force will be greater the greater its velocity.

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* Observation is facilitated by substituting a rectangular vessel, with plane glass sides, for the bulb of the lamp.

7. The above consideration supplies a partial explanation of the phenomenon, for it shows why a bubble may proceed for some distance round the bend of the filament with the impetus acquired during its rise.

Indeed, the necessity for a sufficient gradient of temperature near the wire, if the bubble is to follow it, can be shown in a very simple way.

With a liquid of low boiling point, such as ether, for example, it is only possible to obtain indications of the phenomenon under ordinary circumstances. Thus it is possible to obtain bubbles which will rise along the filament to its summit, and perhaps go a little way beyond, but it is impossible to make them descend very far. The buoyancy exceeds the force pressing the bubble towards the wire, and it escapes to the surface of the liquid.

But if a steeper temperature gradient from the wire to the liquid is made possible, by cooling the ether in a freezing mixture beforehand, it is easy to obtain bubbles which descend as in other liquids of higher boiling points.

Conversely if we take a liquid which shows the phenomenon under ordinary circumstances, we can cause its disappearance by raising the temperature of the liquid, sufficiently, beforehand.

8. Assuming that the variation of viscosity which accompanies the temperature gradient operates in the way indicated above, it remains to consider the origin of the moving force, other than gravity, which acts upon the bubble.

This force must obviously have a considerable component parallel to the wire, and this must act, at every instant, in the direction in which the bubble is moving.

That this moving force depends upon the current strength, and, therefore, upon the temperature gradient, is easily shown. Thus, if the current strength be slowly diminished, after the bubble has formed, the oscillations of the latter gradually diminish in amplitude until the motion extends over only a small arc near the summit of one of the limbs of the filament.

The moving force is now so small that a very small fraction, acting parallel to the wire, of the opposing force due to the buoyancy of the bubble is sufficient to bring it to rest.

9. In attempting to explain how the moving force arises, suppose, for simplicity, that the bubble is momentarily at rest upon a horizontal wire. It will be in a region where the successive filaments of liquid, above and parallel to the wire, are of decreasing temperature. These filaments will be in unstable equilibrium, the upper ones being heavier than the lower. The latter would rise through the former but for the presence of the wire.

Now imagine a small displacement of the bubble along the wire. This will tend to elevate the liquid immediately in front of the bubble and to depress that immediately behind it. To convey roughly what is meant, the case of a sphere moving along the bottom of a horizontal trough containing a layer of water, with a layer of oil above it, may be cited. If the trough has glass sides, the water can be seen to rise in front of the sphere whilst the oil falls in behind the sphere as it moves. This takes place although the oil is much less dense than the water and the surface tension between them is considerable. A similar but more pronounced effect may, therefore, be anticipated in the case under consideration where the upper layers are denser than the lower and surface tension is inappreciable.

It is conceivable that this action once begun might continue of itself and keep the bubble moving forward. But, apart from this possibility, the colder liquid falling in behind the bubble will at once expand owing to its proximity to the wire and will thus tend to push the bubble forward in the direction in which it has begun to move.

The same kind of impulse will be produced in a similar way when the bubble is displaced downwards on a wire which is not horizontal and may be sufficient to enable it to move "against gravity."

In accordance with the facts, the distance through which the bubble is able to move in this way will depend upon the steepness of the temperature gradient, *i.e.*, upon the current flowing through the lamp.

The foot of each limb of the filament is comparatively cold owing to its nearness to the thick leading-in wire. Consequently the downward impulse will rapidly diminish as the bubble nears the end of the wire. The upward influence of gravity* will thus eventually assume predominance, bringing the bubble to rest and then starting it upon its return path.

10. According to the views just expressed, the bubble is continuously removing hotter layers of liquid from the neighbourhood of the wire and replacing them by colder ones. Consequently, in order to dissipate electric energy at a given rate, the temperature of the wire need not be so high when the bubble is present as when it is absent.

To find whether the difference was easily perceptible some observations were made with a platinum filament immersed in turpentine.† A bubble having been formed upon the wire, simultaneous readings of the current through it and the voltage between the terminals were made, as the current was reduced, with the following results :—

Bubble on wire.	
Amperes.	Watts.
2·5	4·25
2·4	3·87
2·3	3·49
2·2	3·18

The bubble disappeared when the current was lowered to 2·2 amperes. The current was then gradually raised to 2·5 amperes again (there being now no bubble present) and simultaneous readings of current and voltage were taken as before :

No bubble.	
Amperes.	Watts.
2·5	4·34
2·4	3·93
2·3	3·55
2·2	3·18

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* In my experiments the upward currents of hot oil referred to by Mr. Crawley were inconspicuous, except near the vertical parts of the filament.

† A large quantity of turpentine was used in order to reduce, as much as possible, fluctuations in the temperature of the liquid as a whole during the course of these observations. Check measurements were made to ensure, for example, that the differences shown in the Tables were not attributable solely to a gradual rise in temperature of the liquid during the observations. From their nature the data are not to be regarded as more than qualitatively correct. They may, moreover, indicate merely the effects of general disturbance (equivalent to stirring) produced by the moving bubble.

From these data it will be seen that, when equal quantities of energy are being dissipated, the current is always greater, and therefore the resistance is always less, when the bubble is present than when it is absent. Since the wire is of platinum, the temperature must be less when the resistance is less.

If the bubble is watched it is seen to be followed by a trail of liquid, evidently of very different density from the main bulk, moving outwards from the part of the bubble furthest from the wire. Such a trail would be formed by hot liquid thrown off by the moving bubble (see also below).

11. It has been inferred (§ 4) that a bubble of vapour cannot remain of constant size except under continuous evaporation and condensation of liquid. This can be demonstrated in the following way:—

When the amplitude of the oscillations of the bubble is continuously reduced in the way described in §8, the bubble frequently becomes so small that it comes to rest before it disappears, by adhering to a minute thread or roughness (visible through a microscope) upon the wire. It is generally possible to adjust the current so that this stationary bubble remains of constant size instead of gradually disappearing. It is then easy to observe that a stream of hot liquid is rising from the side of the bubble remote from the wire.

It is probable that in this case the film of liquid between the bubble and the wire is excessively thin. The central part of the film may even disappear. Liquid will be approaching it continuously owing to capillarity, but may be volatilising at such a rate as to keep the film interrupted at its centre. The wire will tend to become very hot at this point, for it must be remembered that the current through the wire (when a bubble is present) is always such that the wire would become incandescent if the liquid were removed. The evaporation into the bubble near the wire is compensated by an equal condensation at the remote part of the bubble, the temperature being kept below the boiling point here by the mixing of the condensed vapour with the surrounding cooler liquid. This process produces the rising stream.

It will be noticed that the displacement of such a bubble in either direction along the wire would bring fresh liquid over a very hot part of the wire. The sudden heating and expansion of this liquid would provide an impetus tending to move the bubble very rapidly in the direction of displacement.

12. An exhaustive consideration of all possible causes of

motion of the bubble has not, of course, been attempted. It is possible that the explanations put forward above, which are reminiscent of those given in the case of the Trevelyan Rocker, are incomplete. For instance, differences of surface tension due to difference of temperature between the two sides of the bubble may produce an effect which has been disregarded. And it may easily happen that a better way of explaining the phenomena will occur to some observer tempted, by their interesting and possibly instructive nature, to take the small amount of trouble required to produce them.

ADDED OCT. 21, 1915.

Since writing the above account of experiments performed in May of last year,* it has occurred to me that it might be instructive, in experiments like those of §10, to obtain some idea of the temperature of the wire in the different cases. Some additional observations, with a wire similar to that previously used, have therefore been made. The results are tabulated below :—

Amperes.	Volts.	Resistance.	Temperature.
2·85	2·20 (no bubble)	0·772	104·0°C.
	2·17 (bubble)	0·761	99·0°
2·95	2·31 (no bubble)	0·783	109·5°
	2·26 (bubble)	0·766	101·5°

The numbers in the first and second columns are currents and corresponding voltages (mean values) obtained as in §10. The numbers in the third column are the resistances obtained by dividing the volts by the amperes in each case.

To obtain the numbers in the fourth column, the liquid was heated by an external source to about 130°C. It was then allowed to cool slowly, being kept stirred meanwhile. The resistance and temperature of the wire were measured from time to time. The numbers in the fourth column give the temperatures at which the wire had the resistances shown in the third.

From these data it is seen that, both with and without the bubble, the average temperature of the wire is 50°C., or more below the boiling point of the turpentine (approx. 160°C.). The temperature of the bubble itself cannot be below the boiling point. It is thus always much hotter than the liquid which it displaces during its motion. But its temperature is maintained by the wire. Therefore that part of the wire upon which the bubble bears at any instant is much hotter than the rest. It is easy to see how this may occur. The thin film sandwiched between the hot bubble and the wire, no longer able to transfer the heat supplied by the wire to surrounding colder layers, is practically instantaneously raised to the boiling point.* The bubble is maintained by evaporation from it.

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* *See* "Bulletin," Phys. Soc., 1914, p. 44.

These experiments show, perhaps more explicitly than any of the others, where the force propelling the bubble originates.

ABSTRACT.

The first of these experiments was due to Mr. Addenbrooke who, using a 100-volt lamp filled with paraffin oil (after removing the tip) as a convenient high resistance in a 200-volt circuit, noticed that some of the many bubbles forming on the filament behaved in a curious way. Instead of rising at once to the surface from the point at which they formed they ran down the legs of the filament, against gravity, and then escaped at the leading-in wires.

Dr. Smith, led to repeat this experiment by Mr. Crawley, discovered another, more striking, phenomenon. Placing the 100-volt lamp in a 100-volt circuit in series with a variable resistance (conveniently a water-trough) it was found possible, by momentarily cutting out most of the resistance, to obtain a single bubble upon the wire. The behaviour of such a bubble is very interesting to watch. Instead of escaping at either terminal, as in Mr. Addenbrooke's experiment, it travels backwards and forwards between the two, "looping the loops" of the filament in a fascinating way during every journey.

The peculiarities of this phenomenon, which can be obtained with either direct or alternating supply, have been analysed by examining the size and motion of the bubble under various conditions and also by using filaments of different materials and liquids of different boiling points.

It was shown, from the experiments, that a rapid fall of temperature from the wire through the liquid, in the region through which the bubble moves, is an essential condition of the phenomenon, and also, from theoretical considerations, how this condition can be used to explain why the bubble moves in the manner described.

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* In the experiment by Mr. Moss, referred to in § 2, some of the air bubbles being too large did not attach themselves to the wire as intended. Passing across the wire, they rose to the surface of the oil and, bursting there, discharged minute clouds of smoke. The short time during which a film existed upon the wire, while the bubble passed across it, had sufficed to enable the current to heat the film to decomposition.

VII.—*On Obtaining and Maintaining a Bright Hydrogen Spectrum with Special Reference to the* 4,341 *Line.*

By J. Guild, *A.R.C.Sc., D.I.C., F.R.A.S.* (*From the National Physical Laboratory.*)

Received November 18, 1915.

Synopsis.

1. Introduction.
2. Previous Work.
3. Apparatus Employed.
4. Features of Uncondensed Discharge.
5. Effect of Capacity and Inductance.
6. Effects of Impurities.
7. Deterioration of Hydrogen Tubes.
8. Minimising the Deterioration.
9. General Usefulness of Bulb-tube.

1. *Introduction.*

In the system at present adopted for the classification of optical glasses, use is made of the following spectrum lines in terms of which to specify their refractive and dispersive properties :—

Spectrum line.	Wave-length.	Source.
K_α or A′	7,682 Å.U.	Potassium flame.
H_α ,, C	6,563 ,,	Hydrogen vacuum tube.
D_1	5,896 ,,	Sodium flame.
H_β or F	4,861 ,,	Hydrogen vacuum tube.
H_γ ,, G′	4,341 ,,	Hydrogen vacuum tube.

For all ordinary purposes the A′ line is superfluous, and is rarely included in determinations of refractive index. The practical standards for routine work are therefore the sodium line and the C, F and G′ hydrogen lines.

This system has been much criticised,* principally on account of the unsuitability of these lines for accurate work. Of these the G′ is by far the least satisfactory, and has probably been the bane of every observer who has used it in practical optics. Vacuum tube discharges are of small intrinsic brightness at best, and when used in conjunction with a Pulfrich refractometer, which is itself very wasteful of light compared with a spectroscope, it is essential to employ relatively heavy excitation to obtain lines bright enough to give the ease of setting and freedom from eye-strain essential to accurate work. With a current of 15 to 20 milliamperes in a new tube, or one which has been newly re-exhausted, plenty of light is obtained in all the required lines, but the tube deteriorates so rapidly that in a very short time the G′ is hardly visible while the F line has lost much of its initial brilliance. The author has frequently found the G′ of a new or freshly prepared tube disappear completely in the course of an afternoon's work, despite the most rigorous economy in the discharge and the time during which it was running. The chief difficulty, therefore, is not in obtaining sufficient brightness in the required lines but in maintaining it for any length of time, and the object of the present investigation was to determine the conditions governing the intensity of the lines, especially G′, with a view to mitigating as much as possible their rapid deterioration under the influence of the discharge.

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* See, for example, Dr. Martin Lowry, "Proc." Phys. Soc., XXIV., VI., 400; and Lt.-Col. Gifford, "Optician," July 2, 1915; also discussion on same, "Optician," Aug. 27, 1915.

2. *Previous Work.*

With regard to the relative brightness of the lines of the series spectrum of hydrogen some interesting results were described by Mr. H. L. P. Jolley* who measured the energy of the C, F, and G′ lines under certain conditions of discharge with a Rubens thermopile and Paschen galvanometer. Unfortunately, in order to obtain sufficient energy, Jolley was obliged to use heavily condensed discharges at pressures of several centimetres of mercury in water-cooled quartz tubes. He was therefore working under conditions quite outside the limits of ordinary practice, but it is of interest to note that under these conditions the energy becomes more concentrated at the red end of the spectrum as the discharge current or the pressure of the gas is increased. Jolley also measured the total energy of the uncondensed discharge and found it to be very nearly proportional to the discharge current over a considerable range. P. G. Nutting and Orin Tugman† showed that in the case of the uncondensed discharge in hydrogen the energy is more concentrated at the red end of the series spectrum for high currents than for low. Thus, with 380 milliamperes, C was 60 times, F 24 times, and G′ only 12 times as bright as with a current of 20 milliamperes, the pressure being 1 mm. They found that the intensity of the lines at constant current was a maximum at about 1 mm., diminishing as the pressure was altered either above or below that value. There was no selective effect in this case corresponding to that observed by Jolley for condensed discharges.

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* "Phil. Mag.," XXVI. 1913, 801.

† "Bulletin," Bureau of Standards, VII., 1911, p. 49.

G. Stead[*] showed that with hydrogen, in whatever way prepared, the series spectrum is bright at the cathode and faint at the anode, while the secondary spectrum is brightest at the anode. Sir J. J. Thomson[†] also found that the intensity of F relative to that of C was much less near the anode than the cathode.

B. Hasselberg[‡], M. A. Dufour[§] and others have found that the secondary spectrum is favoured by weak and the primary spectrum by strong discharges.

W. E. Curtis[||] states that if hydrogen be thoroughly dried by standing over P_2O_5 for some time, the series spectrum is comparatively feeble. Curtis also experienced difficulty with the rapid deterioration of the series lines when the discharge current was high, a quarter of an hour being sufficient in some cases to necessitate refilling of the tube. To get over this, Curtis employed the elegant device of continuously sucking the gas through his discharge tube from a reservoir at atmospheric pressure, a length of very fine capillary being interposed to maintain the difference of pressure between that of the gas in the reservoir and that in the discharge tube. This appears to have given entire satisfaction for the duration of the longest exposures required.

P. G. Nutting[¶] in a series of Papers dealing with the preponderance of one spectrum over another in a mixture of two spectra treats of the effects of capacity and inductance on the character of the discharge in various gases, including hydrogen. It should be noted that Nutting, following Plücker and Hittorf, uses the terms *primary* and *secondary* in the reverse sense to that of the other authors quoted. Thus the many lined spectrum which appears in the uncondensed discharge in hydrogen at high pressures is termed the *primary* spectrum by Nutting, whereas in those of the other Papers quoted above in which the terms *primary* or *secondary* occur this is referred to as the *secondary* spectrum. The latter practice is the one followed in the present Paper.

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[*] " Proc.," Roy. Soc., A, 85, 1911, p. 393.

[†] " Proc.," Roy. Soc., 18 5, Vol. 58, p. 244.

[‡] " Mem. de l'Acad," de St. Petersburg, VII., Vol. 31, p. 14.

[§] " Ann. de Ch. et de Ph.," (3), 1906, Vol. 9, p. 361.

[||] " Proc.," Roy. Soc., Vol. XC., 1914, p. 605.

[¶] " Bulletin," Bureau of Standards (1), 1904-5, pp. 77, 83, 399.

3. *Apparatus Employed in Present Work.*

All the vacuum tubes used were of the ordinary " H " type with spiral aluminium electrodes. They were, in fact, tubes which had been purchased at various times exhausted and ready for use and which had been laid aside when too unsatisfactory to employ further. The capillaries were about 4 cm. long and 1·5 mm. in diameter. They were used " end on."

To produce the discharge two induction coils were available, one of $2\frac{1}{2}$ in. and the other of 6 in. spark-length, the latter being used in conjunction with a rotary mercury break. This was much steadier and less noisy than the hammer break of the coil.

The Leyden jars used had each a capacity of 0·00075 mfd., while the inductance consisted of a single layer of No. 28 double silk covered copper wire wound on a waxed cardboard cylinder of 15 cm. diameter and 75 cm. in length. Connections from various points of the coil to a rotating dial enabled the inductance to be varied in steps up to about 75 millihenries.

Measurement of the discharge current was effected by passing it through a short straight length of constantin wire (1ω per centimetre) in series with the tube. About 2 mm. above and parallel to this wire a linear thermopile consisting of 20 iron-constantin elements in a length of 1 cm. was mounted. This registered on a Paul semi-pivoted microvoltmeter of 10ω resistance and full-scale reading 0·3 millivolt. This proved a very satisfactory arrangement for the range of current employed, the full deflection being obtained when 45 milliamperes passed through the heater, but it could only be used for uncondensed discharges. If a condenser was employed or if a spark gap was opened in series with the tube, it appeared to be impossible to prevent discharges passing between the heater and the thermopile which vitiated the readings completely. The author is indebted to Mr. A. Campbell for much experienced advice on the measurement of high potential currents.

4. *Features of Uncondensed Discharge.*

The general effects of varying the pressure in a hydrogen vacuum tube on the character of the spectrum are well known. At pressures of 5 cm. or 6 cm. of mercury the energy is almost wholly confined to the many-lined or secondary spectrum, while the lines of the Balmer series are faint and lustreless, G′, the most important from the point of view of this Paper, being scarcely visible. As the pressure diminishes the energy progressively passes from the secondary to the series spectrum, which gradually brightens up. It is not, however, until the pressure is under a centimetre that G′ can be described as good. At 5 or 6 mm. all the lines shine out with a brilliant lustre which continues to improve until about a millimetre is reached. If the pressure is reduced much below a millimetre* the resistance of the tube begins to increase, and the brightness of the lines is diminished.

It will be seen, therefore that the most favourable range of pressure for obtaining a satisfactory G′ line is from 1 mm. to 5 mm. of mercury.

Having exhausted the tube to a pressure within this range, the actual brightness of spectrum obtained will depend on the discharge current, the only limit to its increase being set by the breaking of the tube. Using a water-cooled tube and 6-in. coil, the author was able to obtain a G′ line quite as bright as the violet mercury line given by a particular water-cooled quartz arc taking 6 amperes.

The places where fractures are likely to occur are the capillary and the ends of the tube in the neighbourhood of the electrodes. In order to determine how the heating of these parts depended on the conditions under which the tubes were run, a single thermocouple of copper-German silver was tied firmly to the capillary with cotton thread, so that the junction was above and opposite the middle of the capillary. Suitably shunted, the couple was connected to the Paul micro-voltmeter already mentioned. The reading of the latter indicated on an arbitrary scale the heat developed in the capillary. A similar junction was bound to the wall of the tube near where the cathode enters the glass. By means of mercury cups it was easy to take successive readings of the two couples, and of the current in the tube.

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* The actual pressure at which the resistance of the tube begins to increase depends on the dimensions and on the magnitude of the current. It is supposed to mark the stage when the further extension of the cathode glow is hindered by the walls of the tube.

In Fig. 1 the indications of the two couples are shown as the pressure of the tube is varied. The voltage on the primary of the induction coil was maintained constant throughout.

The curves show that the heat developed in the capillary decreases as the pressure diminishes, falling off very rapidly at low pressures, while the heating of the glass near the electrodes is least at high pressures, rising gradually as the pressure falls. There is a rapid increase below 1 mm.

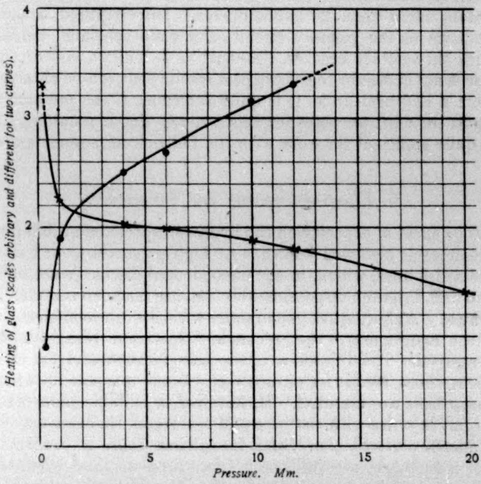

FIG. 1.—HEATING OF TUBE AT DIFFERENT PRESSURES.
(Constant voltage on primary of induction coil.)
● ● ● ● Capillary.
× × × × Glass near negative electrode.

From these results it is clear that the danger of a cracked capillary increases rapidly as the pressure rises, while if the exhaustion is carried much below 1 mm. trouble with the glass near the electrodes may be expected. Hence at pressures of 1 to 3 mm. larger currents can be used with confidence than can safely be employed outside that range.

The author has found that most tubes of the ordinary commercial pattern will stand 30 to 35 milliamperes for a considerable time, while they will take as much as 45 milliamperes for short periods of 30 seconds to a minute, without serious risk, if rests of one or two minutes are allowed.

These currents are well within the capacity of a 6 in. coil. With a 2½-in. coil such as is generally used for vacuum tube work in refractometry, &c., it has not been found possible to obtain more than 20 milliamperes. This required 5 or 6 amperes in the primary circuit, and gave continual trouble with the contact breaker. Nevertheless, while a coil of this size is not sufficient to get the best results that can be obtained from a hydrogen tube, it is quite sufficient, if the pressure is right, for most purposes for which the G′ line is required. It is quite sufficient for work with the Pulfrich refractometer.

5. *Effect of Capacity and Inductance.*

The effect of capacity on the hydrogen spectrum at different pressures is also well known. At high pressures (5 or 6 cm.) the series lines, which, in the uncondensed discharge are faint and dull, brighten up considerably, but are rendered completely diffuse. A short spark gap in series with the tube enhances the effect enormously, the secondary spectrum being almost destroyed. The diffuseness of the lines, unfortunately, renders them wholly useless for refractometry or any purpose for which sharp lines are essential. If, however, a suitable inductance be put in series with the tube and spark gap, the lines may be rendered perfectly sharp, and, though less bright than without the inductance, are still many times more so than when the uncondensed discharge is employed. Moreover, the secondary spectrum is still much enfeebled while any lines due to residual air are quenched.

As the pressure is reduced the enhancing effect of capacity and inductance decreases until at about 1 cm. it is negligible, although it is of interest to note that over a small range the brightness of C may be slightly diminished while that of G′ is appreciably increased. Below this the effect of capacity and inductance is to diminish the brightness of all three lines, though there is still an appreciable increase in the contrast between the lines and their surroundings, due to the partial suppression of the secondary spectrum which appears to take place to some extent even at the lower pressures.

In these experiments it was found that two Leyden jars were distinctly better than one, while three were probably still better, but no improvement was obtained on adding more capacity. Inductances of between 20 and 40 millihenries seemed equally useful.

The effect of inductance on the condensed discharge in hydrogen for a particular pressure is shown very clearly in a photograph illustrating one of the Papers by P. G. Nutting*, referred to in section 2. Unfortunately the pressure is not stated. With the largest inductance employed (about one-twentieth of that used by the author) the series lines are seen to be quite sharp while the background of secondary spectrum is relatively feeble.

The practical importance of these results will be shown in a subsequent section.

6. *Effects of Impurities.*

When reasonable precautions are taken there need be no gaseous impurities present in the tube in sufficient quantity to affect the brightness of the hydrogen lines. It is much more difficult, however, to prevent the presence of traces of mercury in the tube, especially if mercury pumps and pressure gauges are used Mercury is a double nuisance in a hydrogen tube. The slightest trace of it detracts enormously from the hydrogen spectrum† and the violet mercury line at $\lambda=4,359$ is so near G′ that in the field of a Pulfrich refractometer it is difficult to separate the two bands without reducing their brightness considerably. If they are not separated, the mercury band overlaps the critical edge of the hydrogen band and accurate setting is impossible. For these reasons it is essential to keep the tube perfectly free from mercury, and, while it is possible to do this using mercury pumps, it is much safer to use an oil pump and to dispense with a pressure gauge. It is easy to judge from the character of the discharge when the proper stage of exhaustion has been reached.

If a tube shows mercury lines it can be completely cleaned by washing out with strong nitric acid which should be run back and forward through the capillary and allowed to stand for some time in contact with the aluminium electrodes. After rinsing out with distilled water several times the tube should be dried in a hot air oven at about 250°C. The cleaning is facilitated if a temporary opening is made at *b*, Fig. 3. If this is not done it is difficult to get the liquids introduced to the portion *bc* or to get them back again.

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* "Bulletin," Bureau of Standards (1), 1904-5, p. 83.

† P. Lewis, "Astroph. Journ.," 10, p. 137, 1899, has shown that if one molecule of mercury vapour be present for every three thousand molecules of hydrogen, the intensity of the hydrogen lines will be halved.

7. *Deterioration of Hydrogen Tubes.*

When a new tube is run with a current sufficient to give a satisfactorily bright discharge, the character of the discharge rapidly alters. First of all the G′ fades. This is followed less rapidly by the F line and eventually even C loses much of its initial brilliance. The background of secondary spectrum becomes relatively stronger, the positive column loses its red colour, while the sodium lines make their appearance. The tube, in fact, passes inversely through the various stages which may be observed if the pressure of the gas be gradually diminished. The deterioration is, therefore, due to a continual rise in pressure under the influence of the discharge. As an example of the rate of increase, Fig. 2 is of interest. The ordinates represent the pressure in a discharge tube through which a current of 35 milliamperes was running. The abscissæ give the time from the commencement of the test.

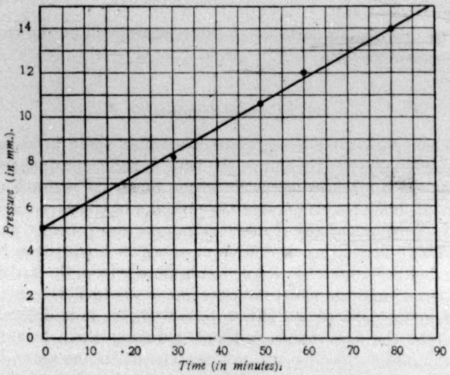

FIG. 2.

On stopping the discharge and allowing the tube to cool the pressure did not alter appreciably.

The increase, which is due to the evolution of hydrogen by the electrodes, is more pronounced in some tubes than in others, but is sufficient in all cases to render the ordinary type of discharge tube wholly useless for any purpose for which the G′ line is wanted, as the necessary current makes the frequency with which re-exhaustion is required extremely troublesome.

8. *Minimising the Deterioration.*

In section 5 it was shown that when the pressure in a discharge tube is under a centimetre of mercury the brightness of the series lines cannot be increased by using capacity and inductance, but that at higher pressures considerable improvement may be effected by this means. This at once suggests the use of capacity and inductance with tubes which have partially deteriorated. With a tube which was so far gone that no trace of the G′ line was visible in the field of a Pulfrich refractometer it was possible by introducing capacity and inductance to obtain a band sufficiently bright to make fairly good settings.

This method, while a very valuable reserve in case of emergency, is not, however, a satisfactory solution of the difficulty, inasmuch as it does not diminish the rise of pressure, which ultimately gets so high that the tube is unusable under any conditions.

Attempts to age tubes by running them with a heavy current for several hours before detaching them from the pump proved useless, as did also attempts to regulate the pressure, by means of charcoal or metallic absorbents. These presented too many difficulties to be practicable.

The attractive method employed by Curtis (*see* section 2) is obviously only feasible for purposes of research and much too cumbersome for use in routine work where the vacuum tube is only an accessory and has to be ready for use when required without any preliminary trouble.

The problem was eventually solved by attaching to the discharge tube a large auxiliary volume. This consisted of a spherical bulb* of about 6 in. diameter and was fitted to the

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*** The bulb can be obtained at trifling cost with neck already drawn out ready to attach at *a* from any manufacturer of X-ray apparatus.**

discharge tube as in Fig. 3. This arrangement enables the capillary to be immersed in a glass water bath if it is desired to run the tube very heavily.

The presence of the auxiliary bulb diminishes the rate of change of pressure due to the evolution of hydrogen in the ratio of the volume of the discharge tube alone to that of the tube plus bulb, *i.e.*, by about 25 cubic cm. to 1,800 cubic cm., o 1:70 approximately. The useful life of the tube is thus prolonged by about 70 times, assuming that no diminution occurs in the rate at which gas is evolved. Any gradual diminution of this rate, were it to occur, would still further prolong the life of the tube. The frequency with which re-exhaustion becomes necessary, even with heavy usage, is thus reduced to within reasonable limits. As a matter of fact, none of the tubes which the author has prepared have yet required refilling, nor do they show any serious evidence of deterioration. One of these, A_5, has been used for practically all the optical glass testing done at the Laboratory in the last four months, while another, A_6, has been used for a large amount of research work sometimes involving continuous action under discharge currents of 20 to 25 milliamperes for several hours on end. As a practical test of the new bulb-tube an ordinary tube, A_7, with no bulb, was exhausted to the same degree as A_6. A discharge of

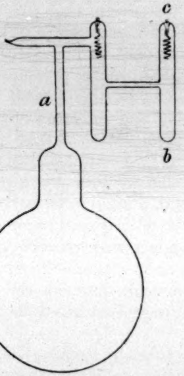

FIG. 3.

20 milliamperes was then run through the tubes in series. At the commencement the discharges were exactly similar, but, at the end of two hours, the intensity of G′ in the spectrum of A_7 had fallen to 0·2 of its initial value and that of F to about 0·4. No change whatever was detected in the case of A_6.

9. *General Usefulness of Bulb-Tube.*

As indicated in the introduction, the work which has been described was rendered necessary by the exigencies of the refractometry of optical glass. The difficulty of obtaining a satisfactory G′ line from ordinary tubes involved considerable loss of time spent in taking a multiplicity of observations, while the strain on the eyes of the observer was a serious matter if much work had to be done at a time. Since the new type of tube was introduced, however, there has never been any difficulty in obtaining a suitable G′ line, and observations at this wave-length are now as easy and accurate as those on any of the other standard lines.

The usefulness of the bulb-tube is not, of course, confined to refractometry. For spectroscopic and spectrographic work the advantages of being able to maintain a vacuum tube discharge of constant character, even under heavy excitation, for considerable periods without external regulation are obvious. If a 6 in. coil is used sufficient G′ light can be obtained from a hydrogen tube for polarimetric and spectrophotometric work. Except in cases where the nature of the gas renders the use of small quantities imperative, the attachment of an auxiliary volume to dilute down changes due to varying pressure or to the development of impurities seems to be an advantageous proceeding in all vacuum tube work.

ABSTRACT.

The Paper treats of the conditions of pressure, discharge, &c., most suitable for the production of a bright hydrogen spectrum, such as is required for refractometry and similar purposes. The rapid deterioration of the tubes with use is shown to be caused by a rise of pressure due to the evolution of hydrogen by the electrodes. The trouble may be obviated by sealing an auxiliary bulb of 1½ or 2 litres capacity to the discharge tube. This reduces the rate of pressure variation and prolongs the useful life of the tube nearly a hundredfold. The use of capacity and inductance is shown to be very helpful with partially deteriorated tubes.

DISCUSSION.

Mr. F. E. **Smith** asked if the hydrogen could not be expelled from the electrodes before sealing off.

Mr. S. D. **Chalmers** said he had had a similar experience with the deterioration of hydrogen tubes. He was surprised that the author found all the lines to be most satisfactory at the same pressure. He had sometimes found it convenient to use different tubes for the C and G′ lines.

Mr. G. H. **Gardiner** mentioned that when taking some photographs of vacuum tube spectra he had been struck with the rapid deterioration of some of the ultra-violet lines. This had been traced to the formation of a scarcely perceptible deposit on the quartz window due to the scattering of the electrodes, and he thought a similar cause might be sufficient to account for the decay of the violet hydrogen line.

Prof. J. W. **Nicholson** thought the Paper, although written from another point of view, formed a useful contribution to the knowledge of the conditions under which different spectra of the same gas were produced. The hydrogen spectrum was a difficult one to deal with, and anything which threw additional light on it was welcome.

Mr. D. **Owen** referred to the rapid rise in the heating of the glass near the electrodes at pressures under 1 mm. What happened at still lower pressures ? Presumably the rise could not go on indefinitely, as, under the conditions of the experiment, the current decreased as the exhaustion progressed.

The **Author**, in reply, said he had tried to get rid of the hydrogen occluded in the electrodes before detaching the tube from the pump but without success. His experience that all the lines attained their maximum brightness at the same pressure was borne out by all other observers who had made quantitative observations. A tube which does not show any G′ may still have plenty of C and F on account both of the greater energy of these lines and of their greater visibility, but he could not conceive of a tube having a usable G′ being deficient in either C or F. It was shown conclusively in the Paper that the deterioration was due to pressure changes. No " imperceptible " deposit could affect lines in the visible spectrum, however effective it might be in the case of those in the ultra-violet. Moreover, no deterioration due to deposits on the glass or to the condition of the capillary would be retarded in the least by the addition of an auxiliary volume. With regard to the heating of the glass, the general form of the curves was easily explained in terms of well-known vacuum tube phenomena. The experiments, however, were intended to give practical rather than theoretical information, and the care expended on them was not such as to justify any conclusions being drawn as to what might happen at pressures below those actually reached.

VIII. *Determination of the Coefficient of Diffusion of Potassium Chloride by an Analytical Method.*

By A. GRIFFITHS, J. M. DICKSON *and* C. H. GRIFFITHS.

RECEIVED JUNE 21, 1915.

§ 1. *Introduction.*

THIS Paper represents an attempt to develop an analytical method of determining the coefficient of diffusion of a salt in water capable of giving consistent and accurate results.

The lower ends of a number of vertical and parallel diffusion tubes end in a reservoir of large capacity containing a solution of potassium chloride. The greater part of the reservoir is above the lower ends of the tubes, and by gravity the solution at the lower ends is kept at an approximately constant concentration. The upper ends of the tubes are covered with a cap provided with an outlet and an inlet tube. Water enters the cap by the inlet tube, and a weak solution containing the diffused salt leaves the cap by the outlet tube. Time, which may be as long as a fortnight, is allowed for the attainment of the steady state, and an individual experiment may last six weeks. The quantity diffused is obtained by chemical analysis.

§ 2. *Theory.*

Let n_0=the concentration at the top of the tubes.
N=the contentration at the bottom of the tubes.
D=the density at the bottom of the tubes.
L=the length of each tube.
k=the coefficient of diffusion.
c=quantity of salt transmitted per unit area.
ρ=density of solution.
n=the concentration of the solution.

Let it be assumed that

$$\rho=1+an,$$

and let

$$b=1-a$$

V=downward velocity of liquid at bottom of tubes.

It can be proved that

$$\frac{-b(N-n_0)}{(v-bc)}+\frac{v}{(v-bc)^2}\log_e\frac{(v-bc)N+c}{(v-bc)n_0+c}=\frac{L}{k}, \quad . \quad . \quad (1)$$

where

$$v=V(1-bN)=V(D-N). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Under the conditions of the experiments of this Paper, by expanding the left-hand side of equation (1) it can be proved that the relation between c and k is represented approximately by

$$\frac{(\mathrm{N}-n_0)}{c}\left\{1-\frac{v(\mathrm{N}-n_0)}{2c}\right\}=\frac{\mathrm{L}}{k}. \quad . \quad . \quad . \quad . \quad (3)$$

Let δ=the ratio of the increment in volume produced to the increment in the mass of salt dissolved for a solution of the strength of that of the reservoir; *i.e.*, it is numerically measured by the increase in volume produced when 1 gramme of salt is dissolved in a solution of the given concentration, the amount of the solution being so great that the addition of the salt makes no appreciable change in the concentration.

Obviously*

$$\mathrm{V}=c\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (2) and (4)

$$v=c(\mathrm{D}-\mathrm{N})\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By substitution of this value of v in (3)

$$k=\frac{\mathrm{L}c}{(\mathrm{N}-n_0)}\times\frac{1}{1-\frac{1}{2}(\mathrm{D}-\mathrm{N})(\mathrm{N}-n_0)\delta} \quad . \quad . \quad . \quad . \quad (6)$$

The term $\frac{1}{2}(\mathrm{D}-\mathrm{N})(\mathrm{N}-n_0)\delta$ has a value small compared with unity, and it is, therefore, unnecessary to determine the value of δ with a high degree of accuracy.

§ 3. *Apparatus and Method.*

A diagrammatic sketch of the final form of the apparatus is shown in Fig. 1. The diffusometer D is placed in a large accumulator tank filled with water. This accumulator tank was fixed in a strong wooden box, the space between it and the box being packed with cork dust. The box was covered with a lid, not shown in the diagram. The whole apparatus was placed in a room kept at a fairly constant temperature by means of an automatically controlled gas stove.

At one time vibration was suspected as a disturbing factor, and to minimise vibration in later experiments the box was suspended by a stout spring, S, and a vane attached to the

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* It may be mentioned that

$$\delta=\left(1-\frac{d\rho}{dn}\right)\Big/\left(\rho-n\frac{d\rho}{dn}\right)$$

$$=[(\rho_1-n_1)-(\rho_2-n_2)]/(n_2\rho_1-n_1\rho_2) \text{ approximately,}$$

when n_1 and ρ_1 and n_2 and ρ_2 are neighbouring pairs of values of ρ and n.

bottom of the box dipped into a viscous liquid. In addition, the diffusometer D was suspended by a weak spring, *s*, from an upright fitted to the box.

Two methods were employed to obtain the slow flow of water. The first method gave a gradually decreasing rate of flow, and was ultimately discarded; the second is suggested in the sketch. A tube, O_2, connected with O_1, the outlet to the diffusometer, passed freely through a hole in the stopper of the tube T, and dipped into liquid kept at a constant level by

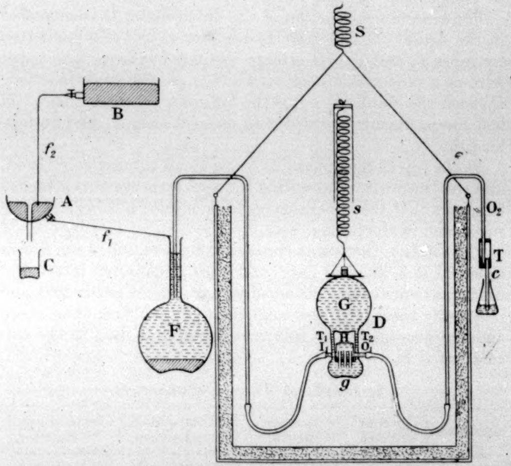

Fig. 1.

means of the overflow tube *c*. The supply reservoir was a large flask, F. To the water was added a trace of copper nitrate to keep down fungoid growths. As all the tubes connected with the diffusometer were wide, it may be assumed that, as a rule, the level of the water in the neck of the flask and that in T were approximately the same. Water was driven at a steady rate from the flask to T by allowing to fall into the flask from a fine capillary tube, f_1, a steady stream of small drops of mercury. The fine capillary tube was attached to a reservoir, A, the mercury in which was kept at a constant level by means of an overflow tube. The supply of mercury was sustained by means of a second reservoir, B, placed at a higher level and giving through the fine capillary f_2 a slightly faster stream of mercury than that from f_1. Cleanliness of mercury from the beginning to the end is necessary for the success of the method.

It may be added that this method of giving a constant flow is self-adjusting so far as the water is concerned. If an obstruction should form, an automatic difference of level will be created and the flow will again become steady.

The general construction of the diffusometer D is suggested in the figure. G and g are two hollow glass bulbs connected by tubes T_1 and T_2. G is large compared with g. The upper part of g possesses a neck on which a diaphragm is inserted; through the diaphragm pass the diffusion tubes (or tube). H is a compartment provided with an inlet tube, I_1, and an outlet tube, O_1.

At the top of the apparatus was a small circular spirit level, and the three wires supporting the apparatus were so attached to screws that the apparatus could be leveled after it had been suspended in the tank.

The solution that came through the outlet tube from T was collected in a weighed flask, and after a measured interval of time was removed and chemically analysed. Usually two, and frequently three, analyses were made of each flask of solution, and the average of the results obtained was used in the calculation of K.

§ 4. *Details of Three Diffusometers.*

Apparatus.	Number of tubes.	Average length.	Total area of cross-section.	Ratio of length to diameter.
α	8	4·8166 cm.	0·7684 sq. cm.	13·9 approx.
β	4	2·0481 cm.	0·3044 sq. cm.	6·6 approx.
γ	1	4·014 cm.	1·768 sq. cm.	2·6 approx.

It may be mentioned that the measurements do not claim to be accurate to the last figures. The value of δ has been taken throughout as 0·45.

The volume of $G_\alpha=580$ c.c. approx.; of $g_\alpha=80$ c.c.; of $G_\beta=660$ c.c.; of $g_\beta=260$ c.c.; of $G_\gamma=680$ c.c.; of $g_\gamma=360$ c.c.

§ 5. *Results.*

Details of experiments are given in Table I. In the case of experiments α_1, α_2, α_3, β_1 and β_2 the first method of obtaining

TABLE I.

Experiment.	Interva's in hours.	Weight of flow in.gms.	Av.temp. during interval.	N.	n_0.	${}_nK_N$ during interval.	${}_nK_N$ average from start.
a_1	19·18	97·03	17·2°C.	0·2237	0·0004999	...	$1{\cdot}639\times10^{-5}$
	28·32	96·02	17·2°C.	...	0·0004985	...	$1{\cdot}655\times10^{-5}$
	24·52	97·36	17·2°C.	...	0·0004990	...	$1{\cdot}641\times10^{-5}$
	23·83	95·37	17·2°C.	...	0·0005029	...	$1{\cdot}643\times10^{-5}$
	23·75	94·77	17·2°C.	...	0·0005135	...	$1{\cdot}642\times10^{-5}$
Av. temp., 17·2	28·8	115·93	17·3°C.	...	0·0005125	...	$1{\cdot}650\times10^{-5}$
a_2	74·33	63·13	17·6°C.	0·2238	0·002384	$1{\cdot}668\times10^{-5}$	$1{\cdot}668\times10^{-5}$
	99·97	74·70	17·7°C.	...	0·002699	$1{\cdot}680\times10^{-5}$	$1{\cdot}674\times10^{-5}$
	89·04	71·96	17·8°C.	...	0·002603	$1{\cdot}735\times10^{-5}$	$1{\cdot}693\times10^{-5}$
	71·53	56·54	17·8°C.	...	0·002504	$1{\cdot}632\times10^{-5}$	$1{\cdot}681\times10^{-5}$
	97·92	75·26	17·8°C.	...	0·002715	$1{\cdot}724\times10^{-5}$	$1{\cdot}690\times10^{-5}$
Av. temp., 17·7	167·3	134·67	17·8°C.	...	0·002569	$1{\cdot}706\times10^{-5}$	$1{\cdot}693\times10^{-5}$
a_3	56·39	47·72	17·7°C.	0·2238	0·002397	...	$1{\cdot}671\times10^{-5}$
	69·6	68·39	17·7°C.	...	0·002435	...	$1{\cdot}837\times10^{-5}$
	93·69	73·18	17·8°C.	...	0·002580	...	$1{\cdot}761\times10^{-5}$
	72·09	58·85	17·8°C.	...	0·002553	...	$1{\cdot}760\times10^{-5}$
	96·36	77·42	17·9°C.	...	0·002545	...	$1{\cdot}734\times10^{-5}$
	68·47	53·65	17·9°C.	...	0·002591	...	...
Av. temp., 17·8	123·7	94·79	18·0°C.	...	0·002656	...	$1{\cdot}714\times10^{-5}$
${}_2\alpha_1$	71·33	30·8940	18·4°C.	0·2237	0·004785	$1{\cdot}708\times10^{-5}$	...
	125·75	55·8370	17·9°C.	...	0·004396	1·675	...
	168·00	79·1620	17·7°C.	...	0·004175	1·621	...
Av. temp., 17·8	166·00	78·5630	17·8°C.	...	0·004378	1·708	$1{\cdot}672\times10^{-5}$
${}_2\alpha_2$	144·7	57·4205	20·3°C.	0·0037	0·005737	$1{\cdot}873\times10^{-5}$	...
Av. temp., 20·4	382·5	144·6850	20·5°C.	...	0·005560	$1{\cdot}734\times10^{-5}$	$1{\cdot}772\times10^{-5}$
β_1	74·01	56·42	17·7°C.	0·2238	0·002609	...	$1{\cdot}759\times10^{-5}$
	74·39	57·19	17·8°C.	...	0·002591	...	$1{\cdot}760\times10^{-5}$
	98·9	75·10	18·0°C.	...	0·002511	...	$1{\cdot}730\times10^{-5}$
	89·0	68·14	18·1°C.	...	0·002516	...	$1{\cdot}723\times10^{-5}$
	71·5	53·54	18·1°C.	...	0·002527	...	$1{\cdot}713\times10^{-5}$
	97·8	64·90	18·1°C.	...	0·002776	...	$1{\cdot}697\times10^{-5}$
Av. temp., 17·9	167·2	105·14	18·0°C.	...	0·002961	...	$1{\cdot}685\times10^{-5}$
β_2	46·86	53·64	18·7°C.	0·2237	0·001714	$1{\cdot}728\times10^{-5}$	$1{\cdot}728\times10^{-5}$
	114·4	124·00	18·8°C.	...	0·001793	1·713	1·717
	506·2	52·34	18·9°C.	...	0·001865	1·698	1·712
	94·36	94·70	18·9°C.	...	0·001905	1·685	1·702
	71·44	68·97	18·9°C.	...	0·001977	1·682	1·700
	96·81	90·62	19·0°C.	...	0·002076	1·712	1·702
Av. temp., 18·9	73·18	66·41	19·1°C.	...	0·002221	1·775	1·712
${}_2\gamma_1$	93·4	40·2071	17·7°C.	0·2237	0·01191	$1{\cdot}59\times10^{-5}$	...
	115·67	49·2115	17·7°C.	...	0·01210	1·59	...
	148·33	64·3615	17·4°C.	...	0·01162	1·56	...
Av. temp., 17·5	239·67	100·7215	17·4°C.	...	0·01205	1·57	$1{\cdot}58\times10^{-5}$
${}_2\gamma_2$	117·33	74·2450	19·2°C.	0·2237	0·008740	$1{\cdot}76\times10^{-5}$	...
	119·80	78·0071	18·6°C.	...	0·008319	1·65	...
	98·00	63·7300	18·3°C.	...	0·008545	1·70	...
Av. temp., 18·7	92·30	60·1220	18·7°C.	...	0·008660	1·72	$1{\cdot}71\times10^{-5}$
${}_2\gamma_3$	96·33	47·3520	20·7°C.	0·2237	0·01251	$1{\cdot}91\times10^{-5}$	...
	240·00	117·6237	20·7°C.	...	0·01195	1·82	...
	143·00	73·5120	20·7°C.	...	0·01169	1·86	...
Av. temp., 20·8	144·20	74·2810	21·2°C.	...	0·01149	1·83	$1{\cdot}85\times10^{-5}$

the flow was employed. In the case of β_2 the anti-vibrator was employed. In the case of experiments ${}_2\alpha_1$, ${}_2\alpha_2$, ${}_2\gamma_1$, ${}_2\gamma_2$ and ${}_2\gamma_3$ both the improved method of obtaining the flow and the anti-vibrator were employed. The experiments naturally fall into four groups, the results of which are summarised in Table II. The coefficient of diffusion at 18°C. (*i.e.*, k_{18}) is obtained with the aid of a formula kindly deduced for the authors by Mr. B. W. Clack—viz., $k_t = k_{18}[1+0{\cdot}023(t-18)]$. This equation is intended to apply to a 2·7 normal solution, which is little different from the 3N solution studied in this Paper. Mr. Clack informs the authors that the most probable value of k_{18} from his experiments (including his latest) is $1{\cdot}532 \times 10^{-5}$; thus the value of k_{18} ($1{\cdot}684 \times 10^{-5}$) given by the authors' analytical method is 10 per cent. greater than that given by Mr. Clack. The experimental conclusion of this Paper may be stated as follows: Assuming a linear relationship between the coefficient of diffusion and the temperature over the small range from 17·2°C. to 20·4°C., it is justifiable to co-ordinate the average of the temperatures and the average value of the coefficients; this gives that in the case of a solution containing 0·2237 grammes of potassium chloride to the cubic centimetre (a 3N solution) the "mean diffusivity" with respect to water is $1{\cdot}703 \times 10^{-5}$ (C.G.S. units) at a temperature of 18·5°C.

TABLE II.

Experiment.	Rate of flow in c.c. per hour.	Temp.	k.	k_{18}.	k_{18}.
α_1	4·020	17·2°C.	$1{\cdot}65 \times 10^{-5}$	$1{\cdot}681 \times 10^{-5}$	$1{\cdot}702 \times 10^{-5}$
α_2	0·794	17·7°C.	$1{\cdot}693 \times 10^{-5}$	$1{\cdot}703 \times 10^{-5}$	
α_3	0·816	17·8°C.	$1{\cdot}714 \times 10^{-5}$	$1{\cdot}722 \times 10^{-5}$	
${}_2\gamma_1$	0·463	17·8°C.	$1{\cdot}672 \times 10^{-5}$	$1{\cdot}680 \times 10^{-5}$	$1{\cdot}680 \times 10^{-5}$
${}_2\alpha_2$	0·382	20·4°C.	$1{\cdot}772 \times 10^{-5}$	$1{\cdot}680 \times 10^{-5}$	
β_1	0·931	17·9°C.	$1{\cdot}685 \times 10^{-5}$	$1{\cdot}689 \times 10^{-5}$	$1{\cdot}683 \times 10^{-5}$
β_2	1·003	18·9°C.	$1{\cdot}712 \times 10^{-5}$	$1{\cdot}677 \times 10^{-5}$	
${}_2\gamma_1$	0·428	17·5°C.	$1{\cdot}57 \times 10^{-5}$	$1{\cdot}588 \times 10^{-5}$	$1{\cdot}670 \times 10^{-5}$
${}_2\gamma_2$	0·641	18·7°C.	$1{\cdot}71 \times 10^{-5}$	$1{\cdot}684 \times 10^{-5}$	
${}_2\gamma_3$	0·498	20·8°C.	$1{\cdot}85 \times 10^{-5}$	$1{\cdot}738 \times 10^{-5}$	

§ 6. *Critical Consideration of the Results.*

Much of the work of this Paper was done in co-ordination with Mr. B. W. Clack; and apparatus β and apparatus γ were made because apparatus α gave results so different from his.

In all the calculations the value n_0 has been assumed to be that of the solution which comes from the diffusometer. In the case of the α and β experiments n_0 is so small that the assumption can produce no error of importance. The apparatus γ was made so as to include a diffusion tube which should be a close approximation to one used largely by Mr. Clack.* In the authors' experiments, however, involving as they do a continuous stream of water through the apparatus, the wide single tube gives less consistent results than the batteries of narrow tubes. It has been suggested to the authors that there may be an error due to a flow down certain tubes and up others. That this is extremely unlikely is proved by some earlier work† of one of the authors. Also the substantial agreement of the results given by the three pieces of apparatus, with various rates of flow, suggest that the flow has not a considerable influence. There is a possibility of a small error due to the reservoir G not being large enough to justify the assumption that the concentration at the bottom of the diffusion tubes is constant; but the results of Table I. certainly show no signs of a diminution in the calculated values of k which would result from a fall in the concentration. Taking the worst possible supposition—namely, that the solution in G continues homogenous throughout as it diminishes in concentration—it can be shown that the maximum error in the average value of k which could occur in an experiment lasting a month, in the case of the α and the β apparatus would be about 0·4 per cent., and in the case of the γ apparatus about 1 per cent. In practice, owing to the tendency of the lighter solutions to ascend to the top of the reservoirs, and owing to the time-lag in the diffusing power of a tube, the percentage errors will be much less than those calculated. Because perhaps of a variable amount being left in the compartment H the ratio between the quantity diffused and the time is not so constant as the corresponding ratio in Mr. Clack's experiments; nevertheless, the close agreement between the averages of α, β and γ prove that the results are not unworthy of consideration. And it would appear that there is almost certainly some, as yet unknown, factor or factors operating either in Mr. Clack's method, or in the analytical method described in this Paper, to which the consistent difference between the results obtained by the two methods must be attributed.

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* B. W. Clack, p. 43, "Proc." Phys. Soc., Vol. XXIV., Part I., December, 1911.

† A. Griffiths, p. 537, "Phil. Mag.," June, 1899. *It may be mentioned that the word "not" should appear before "appreciable" in the last line of the page.*

ABSTRACT.

This Paper represents an attempt to develop an analytical method of determining the coefficient of diffusion of a salt in water capable of giving consistent and accurate results.

The lower ends of a number of vertical and parallel diffusion tubes end in a reservoir of large capacity containing a solution of potassium chloride. The greater part of the reservoir is above the lower ends of the tubes, and by gravity the solution at the lower ends is kept at an approximately constant concentration. The upper ends of the tubes are covered with a cap provided with an outlet and an inlet tube. Water enters the cap by the inlet tube, and a weak solution containing the diffused salt leaves the cap by the outlet tube. Time, which may be as long as a fortnight, is allowed for the attainment of the steady state, and an individual experiment may last six weeks. The quantity diffused is obtained by chemical analysis. In the case of a solution containing 0·2237 gramme of potassium chloride to the cubic centimetre (a 3N solution) the "mean diffusivity" with respect to water is $1{\cdot}703 \times 10^{-5}$ (C.G.S. units) at a temperature of 18·5°C.

DISCUSSION.

Mr. B. W. CLACK said that the difference of 10 per cent. between the authors' results and those obtained by him was not nearly so great as the discrepancies between the results of other workers on similar solutions. He showed slides containing the tabulated results of other observers for solutions of KCl and NaCl. These differed from one another by 20 to 30 per cent. He believed Dr. Griffiths had had some difficulty at first in the analysis of the dilute solutions. The method by which he had overcome this was, he thought, noteworthy.

Dr. S. W. J. SMITH said he was interested in diffusion from the point of view of electrolytic phenomena. The way in which the diffusion depends on the concentration for different salts had an important bearing on the electrolytic behaviour of dilute solutions.

Dr. T. BARRATT asked if variations of temperature might not account for the discrepancy between the authors' results and those of Mr. Clack. The temperature coefficient appeared to be about 7 per cent. for 3°C. Was it certain that in both methods the temperature was maintained constant to within this amount for the periods of six weeks or so required for an experiment? There was another effect of temperature variations Any expansion of the solution in the reservoir had to take place through the diffusion tubes, and this would affect the results very seriously.

Dr. GRIFFITHS, replying for the authors, said that the temperature had been kept constant to within 0·5°C. He had gone into all the possible errors due to temperature variations and they were not comparable with the 10 per cent. in question. His convective method gave results about 4 per cent. lower than the analytical method.

IX.—*An Apparatus for Evaluating Elliptic Integrals. By* A. F. RAVENSHEAR.

COMMUNICATED BY R. J. SOWTER.

RECEIVED NOVEMBER 23, 1915.

IN this apparatus, graphs of the three elliptic integrals can be described by mechanical means, and the value of the integral between any assigned limits found by measurement of the ordinates of the graph.

The principle of the apparatus is to use a hatchet scriber, which is controlled as regards direction, but is otherwise free to move anywhere over the surface of the paper. The hatchet cuts slightly into the paper, and as it moves makes a trace, which is the required graph. If the direction of the hatchet is kept constant, the trace is a straight line, but if the direction is subjected to a continuous change, the trace is a curve to which the hatchet is always tangent.

The graphs are made with reference to rectangular coordinates, the hatchet being directed so that the tangent of its inclination to the axis of X is always equal to the function of the abscissa (θ), under the sign of integration.

The integrals are dealt with in Legendre's form. Thus, taking the third integral as an example, we have to consider

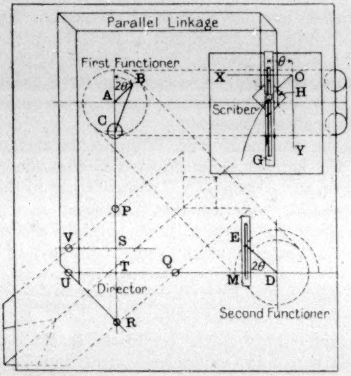
$$\Pi(a, c, \theta)=\int\frac{d\theta}{(1+a\sin^2\theta)\sqrt{1-c^2\sin^2\theta}}.$$

This is treated subject to the conditions that θ is limited to values from 0 to $\pi/2$, c to values from 0 to 1, and $(1+a\sin^2\theta)$ is always positive. These conditions cover all cases which can arise in dynamical and physical problems, and the resulting integrals are all finite.

I. THE CHIEF PARTS OF THE APPARATUS.

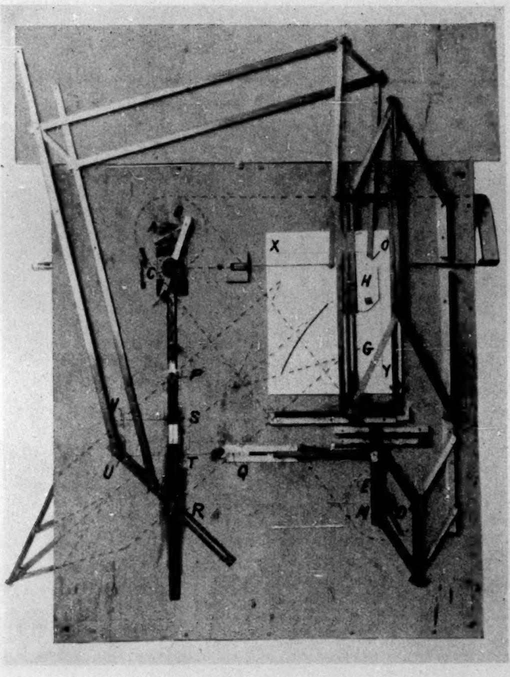
The apparatus comprises five principal parts, supported partly above and partly below a rectangular board. In the right-hand top quarter is the hatchet scriber and its immediate accessories; in the left-hand top quarter the first functioner; in the right-hand bottom quarter the second functioner; in the left-hand bottom quarter a multiplying linkage and the director; and, lastly, extending from the director round the first functioner to the hatchet, a parallel linkage which controls the direction of the hatchet without otherwise restricting its movement.

1. *The Hatchet and its Immediate Accessories.*—The hatchet is on the underside of a plate H, capable of sliding freely along a guide G in the direction of the axis of Y, which guide can also move always parallel to itself in the direction of the axis of X. This guide is connected to a band passing over a pulley in the first functioner, so that a crank arm, AB, in the latter turns through two right angles, while the guide makes a full traverse of a length $\pi/2$.



2. *The First Functioner.*—In the first functioner, the crank arm, AB, mentioned above, forms one side of a variable triangle with a fixed base, AC, the length of the arm and the base being adjustable according to the value of the parameter c, so that the third side of the triangle, BC, always has the value $\sqrt{1-c^2\sin^2\theta}$, where θ is half the angle swept out by the crank arm. By flexible transmission means, a slider, P, in the director is moved so that its distance from a certain fixed point, S, is always made equal to BC.

3. *The Second Functioner.*—In the second functioner another crank arm, DE, is made to turn at the same rate as the crank


A
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T
Q
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E
M
D

To face p. 82.

arm, AB, in the first functioner. The length of this arm is adjustable according to the value of the second parameter, a, in the third integral, and from this arm is operated a second slider, Q, so that its distance from a fixed point T is always equal to $(1+a \sin^2\theta)$, where θ is half the angle swept out by the arm.

4. *The Multiplying Linkage and the Director.*—Under the board is a linkage which connects the first two sliders, P and Q, to a third slider, R, in such manner that the latter is moved when one or both of the first two sliders move so that its distance from the fixed point T is always equal to the product, PS×TQ, of the distances of the other two sliders from their fixed points. On the top of the board is the director link, UR. This can be pivoted at either of the two fixed points, U or V, at unit distances respectively from T and S. When pivoted at V, the director link is guided by the first slider P, and when pivoted at U by the third slider, R, so that the tangent of its inclination to the axis of X is either

$$+\sqrt{1-c^2 \sin^2\theta}, \text{ or } -(1+a \sin^2\theta)\sqrt{1-c^2 \sin^2\theta}.$$

5. *The Parallel Linkage.*—This is a linkage which extends from the director link to the hatchet plate. Its attachment to the hatchet plate can be altered so that the hatchet can be placed either parallel to the director link or at right angles to it. The linkage maintains this relationship between the hatchet and the director link, but leaves the hatchet otherwise free. By these means the direction of the hatchet is controlled so that the tangent of its inclination to the axis of X is $\sqrt{1-c^2 \sin^2\theta}$ when the hatchet is kept parallel to VP, or $1/(1+a \sin^2\theta)\sqrt{1-c^2 \sin^2\theta}$, when the hatchet is kept at right angles to UR. For each point in the graph, taking the third integral as example, we therefore have

$$\frac{dy}{d\theta} = \frac{1}{(1+a \sin^2\theta)\sqrt{1-c^2 \sin^2\theta}},$$

whence

$$y = \int \frac{d\theta}{(1+a \sin^2\theta)\sqrt{1-c^2 \sin^2\theta}}.$$

II. THE MANNER OF USING THE APPARATUS.

1. To draw the graph of the third integral for given values of the parameters, a and c, the crank arm, AB, in the first

functioner is set to a length $\frac{1}{2}-\frac{1}{2}\sqrt{1-c^2}$, and the block, C, through which passes the connecting-rod, BC, forming the third side of the variable triangle, is set so that its distance from the crank centre is $\frac{1}{2}+\frac{1}{2}\sqrt{1-c^2}$. The crank arm, DE, in the second functioner is set at $\frac{a}{2}$, the movable parts placed in the starting position, and the second slider, Q, is set at unit distance from the fixed point T. When this has been done, the first slider, P, is adjusted to unit distance from its fixed point, and the director link is pivoted at U and connected to the third slider, R. The parallel linkage is next connected with the hatchet plate so that the hatchet is at right angles to the director link. The hatchet is then pressed firmly on the card by the right hand, and the guide is caused to traverse by pulling with the left hand on a cord provided for the purpose, the hatchet plate being assisted in its movement in the direction of its length by the pressing hand.

2. The graph of the first integral is produced in exactly the same way as that of the third integral, after the crank arm, DE, has been set at zero, which has the effect of making the factor $(1+a\sin^2\theta)$ permanently unity.

3. To describe a graph of the second integral the director link is pivoted at V and connected to the first slider, P, and the hatchet is set parallel to the director link.

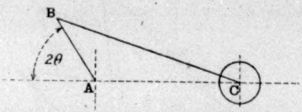
4. All the graphs of the second integral lie between the curve $y=\sin x$ and the straight line $y=x$, and the ordinates consequently never exceed $\frac{\pi}{2}$ in length. But the graphs of the first and third integrals are not confined within this region, and y in these cases may have large values, exceeding the limit fixed by the size of the apparatus. In such a case the graph may be completed by a simple device. When the hatchet plate reaches the upper end of the guide, the apparatus is stopped and held while the scriber is lifted slightly from the card and slid back along the guide towards the axis of X. This produces no effect upon its direction, and the graph can be continued from the new starting point merely displaced a distance equal to the displacement of the scriber.

III. THE GEOMETRY OF THE MECHANISMS.

1. *The First Functioner.*—A crank arm, AB, turns about A, and the connecting-rod, BC, slides through a block which can

turn about C. The length of AB and of AC are both adjustable, and are given the following values :

$$AB=\tfrac{1}{2}-\tfrac{1}{2}\sqrt{1-c^2}\,;\ AC=\tfrac{1}{2}+\tfrac{1}{2}\sqrt{1-c^2}.$$

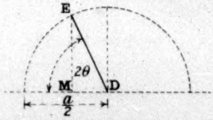


Hence, $BC=\sqrt{AB^2+Ac^2+2AB\,.\,AC\cos 2\theta}$

$$=\sqrt{(\tfrac{1}{2}-\tfrac{1}{2}\sqrt{1-c^2})^2+(\tfrac{1}{2}+\tfrac{1}{2}\sqrt{1-c^2})^2+2(\tfrac{1}{2}-\tfrac{1}{2}\sqrt{1-c^2})(\tfrac{1}{2}+\tfrac{1}{2}\sqrt{1-c^2})\cos 2\theta}$$

$$=\sqrt{1-c^2\sin^2\theta}.$$

2. *The Second Functioner.*—In this the pin on the crank arm, DE, engages with a movable guide, EM, which moves always parallel to the axis of Y, which guide is connected to the slider, Q. Since the slider, Q, is at starting at unit distance from T :



$$TQ=1+DE\text{ vers }2\theta.$$

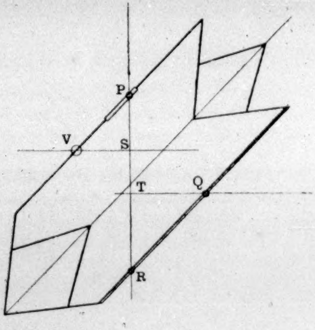
Since DE is made $\frac{a}{2}$,

$$TQ=1+\frac{a}{2}(1-\cos 2\theta)$$

$$=1+a\sin^2\theta.$$

3. *The Multiplying Linkage.*—In this, a pair of bars, VP and RQ, are connected by links in such manner that while they are free to approach and recede one from the other they are kept parallel. One of them is pivoted at the fixed point, V, and

they have sliding connections with the movable sliders, P, Q and R.



By similar triangles

$$\frac{TR}{TQ}=\frac{PS}{VS}.$$

But VS is unit length

$$\therefore\ TR=PS\,.\,TQ.$$

ABSTRACT.

The apparatus produces by mechanical means a graph of the integral in rectangular co-ordinates. The graph is made by a hatchet scriber which is controlled as regards direction, but is otherwise free to move anywhere over the surface of the paper. Taking the third integral as an example.

$$\Pi(a, c, \theta)=\int\frac{1}{(1+a\sin^2\theta)\sqrt{1-c^2\sin^2\theta}}d\theta.$$

The apparatus comprises (1) the scribing appliance ; (2) a mechanism which evaluates $\sqrt{1-c^2\sin^2\theta}$, where θ is the value of the abscissa of the middle point of the hatchet ; (3) a mechanism which evaluates $(1+a\sin^2\theta)$; (4) a multiplying linkage which determines a length equal to the product $(1+a\sin^2\theta)\sqrt{1-c^2\sin^2\theta}$; and (5), a director which is variably inclined to the axis of X so that the tangent of its inclination is negative and equal to the abovementioned product. By a parallel linkage, a line in the hatchet

plate at right angles to the hatchet is kept parallel to the director, so that the hatchet has an inclination φ to the axis of X such that

$$\tan\varphi=\frac{1}{(1+a\sin^2\theta)\sqrt{1-c^2\sin^2\theta}}.$$

Since the hatchet is always tangent to the graph which it describes, $dy/dx=\tan\varphi$, whence

$$y=\int\frac{1}{(1+a\sin^2\theta)\sqrt{1-c^2\sin^2\theta}}d\theta.$$

By suitable adjustments the apparatus deals in a similar way with the first and second integrals.

DISCUSSION.

Dr. A. RUSSELL thought the instrument was very ingenious and likely to be of the greatest utility. The third elliptic integral was of frequent occurrence in electrical engineering and in hydrodynamics, and an apparatus for its easy evaluation would be welcomed by many.

X. *On a General Bridge Method for Comparing the Mutual Inductance Between Two Coils with the Self Inductance of One of Them.* *By* CHARLES H. LEES, *D.Sc.*, *F.R.S.*

RECEIVED JANUARY 13, 1916.

1. When a resistance bridge for the comparison of the mutual inductance between two coils with the self-inductance of one of them has been set up and balanced for steady currents, it is very often found that no inductive balance can be obtained with the form of bridge adopted, or with the values of the resistances of the ratio arms which have been used. Another pair of values for the resistances of the ratio arms or another form of bridge has to be substituted, balanced for steady currents and an induction balance again attempted. To get rid of this waste of time I have introduced into my laboratory the bridge arrangement shown in Fig. 3, which allows an induction balance to be obtained with the ratio arm used in the steady balance whatever may be the relation between the inductances of the coils. If, further, the routine given in section 5 be followed no waste observations are made.

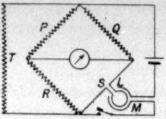


FIG. 1.
MAXWELL.

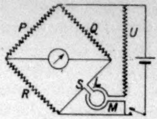


FIG. 2.
BRILLOUIN.

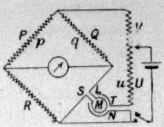


FIG. 3.

2. In Maxwell's form of bridge,* Fig. 1, after the balance for steady current has been obtained, the shunting resistance T is adjusted till there is no throw of the galvanometer on making or breaking the cell circuit. With the resistances and inductances shown in the figure we then have

$$L/M = -\{1+Q/P+(Q+S)/T\}.$$

This is a continuous induction balance; that is, it holds however the E.M.F. applied to the bridge is varied.

From the form of the expression for L/M it is evident that the method is only applicable to cases in which the mutual inductance between the coils is less than about half the self-inductance of the coil in the bridge arm.

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* Maxwell. "Electricity and Magnetism." 2nd edition. Vol. I., pp. 365-7.

3. To get over this difficulty Brillouin* arranged the coils as in Fig. 2. When the bridge is balanced for steady currents the condition for the inductive balance is

$$L/M = -(Q+S)/(T+U).$$

This balance is not a continuous but an aggregate or integral one; that is, the total flow of electricity through the galvanometer from one steady state of distribution of currents in the arms of the bridge to another steady state is zero.

When M is large compared to L it is always possible to get an inductive balance by increasing U whatever values of P and Q have been used in getting the steady balance. But if M is small compared to L no value of U will give an inductive balance unless Q has been taken large enough. In practice this often leads to waste of time in rebalancing the bridge for steady currents with larger values of Q before an induction balance can be secured, or to the bridge being changed to Maxwell's form.

4. The arrangement I have adopted is shown in Fig. 3. The resistances PQR of the usual form of resistance box are supplemented by a second box V, U, through which the second coil is connected to the bridge. The cell is shown connected to an intermediate point of this resistance, but in practice it is connected to one end or the other, that is, either $U=0$ or $V=0$.

With the connections as shown in the figure, the resistances PQR, &c., carrying the currents pq, &c., we have for no current through the galvanometer $\boldsymbol{r}=p$, $s=q$,

$$\begin{aligned}&Pp=Qq,\\&(P+R)p=(Q+S+LD)q+MDu,\\&(P+R)p+V(p+q)=(T+U+ND)u+MDq,\end{aligned}$$

where $D=d/dt$.

On eliminating q and u from these equations we get

$$\begin{aligned}&(T+U)\{P+R-(Q+S)(P/Q)\}p\\&\qquad-[\{(P+R+V+V(P/Q)\}M+(T+U)(P/Q)L\\&\qquad\qquad-\{P+R-(Q+S)(P/Q)\}N]Dp\\&\qquad\qquad\qquad-(P/Q)(LN-M^2)D^2p=0.\dagger\end{aligned}$$

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* Brillouin. "Annales de l'Ecole Normale." 11, p. 339 (1882).

† I have to thank Mr. D. Owen, B.Sc., for calling my attention to the omission of LN from the last term of this equation.

For a steady current balance we have, therefore,

$$(P+R)/(Q+S)=P/Q, \text{ that is } R/S=P/Q.$$

For an aggregate or integral balance for changes from one steady state to another we have

$$\{P+R+V(P+Q)/Q\}M+(T+U)(P/Q)L - \{P+R-(Q+S)(P/Q)\}N=0,$$

which reduces on introducing the condition for steady balance to

$$L/M=-\{Q+S+(1+Q/P)V\}/(T+U).$$

For continuous balance for all changes of E.M.F. on the bridge $LN-M^2=0$, a condition which is not satisfied unless there is no magnetic leakage between the coils. The balance, like Brillouin's, is in general an aggregate or integral one only. For a galvanometer of period not excessively short Allen* has shown that in most practical cases an aggregate balance introduces no appreciable unsteadiness of the needle.

5. In the practice of the method P and Q are the proportional arms of a resistance bridge box, such as the Post Office box, and should be of the same order of resistance as that of the coil whose self-inductance is to be compared, but need not be equal. The coil of resistance S is placed in the open arm of the bridge. In boxes in which the galvanometer leads are connected to the ends of P and Q the final adjustment of the third arm R to give a balance for steady currents may be made by inserting between P and R a short length of resistance wire and altering the length till R is increased by the necessary fraction of an ohm. The actual resistance of the wire may be ascertained by observing the deflections of the galvanometer for the nearest integral ohm too small and that too great and taking proportional parts. If the connections of the keys of the box do not allow a wire to be inserted in this place, a corresponding short length may be put in series with the coil S and its value calculated by taking deflections in the same way. The second coil should be connected through a second resistance box VU to those terminals of the bridge to which the cell is usually attached, and the cell in the first instance connected to the same two terminals. The steady balance is then obtained by taking out the infinity plug at U, making the cell circuit before the galvanometer circuit, and adjusting R by means of the plugs and the wire till the deflection of the galvanometer is reduced to zero. If the drift of the value of R

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* Allen. "Phil. Mag." 25, p. 534 (1913).

for a balance is considerable, the heating of the coil S owing to the current in the bridge must be reduced by inserting a resistance in the cell circuit.

The trouble due to this drift is least when the inductive balance is obtained on breaking the cell circuit rather than on making. The direction and magnitude of the throw of the galvanometer on breaking the cell circuit should be noticed. This direction is that of the self-inductance throw. Now insert the infinity plug in U so that the mutual inductance comes into play, and again notice the direction and magnitude of the throw. If the second or composite throw is greater algebraically than the first or self-inductance throw the second or mutual inductance coil must have its connections to the bridge reversed. If the composite is less algebraically than the self throw, the connections are right. If the composite throw is zero we have a direct balance. If the composite throw is of opposite sign to the self throw the resistance U should be increased till the composite throw becomes zero, V being kept zero. This is the Brillouin arrangement. If the composite throw is in the same direction as, but less than, the self, transfer the cell lead to the U end of the resistance box, thus making U zero, and adjust V till the throw is zero. This is the new arrangement. None of these alternatives require the original steady balance to be disturbed, and by following the routine suggested there is no time wasted in useless observations, whatever the quotient of L by M may be.

The following example* illustrates the method :—

Inside coil L in bridge arm. $P=Q=100$ ohms.

Steady balance with $V=0$, $U=\infty$. With $R=77$ deflection 17·7 left, R=76, 16·1 right.

Hence R for balance=76·48 ohms. Wire resistance adjusted to give balance.

Induction balance. Throws on breaking cell circuit.

$V=0$, $U=\infty$, self 25 left ; $U=0$, composite off scale left.

Connections of mutual coil reversed ; composite 4·3 left.

Hence U made=0 and V adjusted till with $V=22$ ohms throw zero. T found 129·7 ohms.

Hence $L/M=-220{\cdot}48/129{\cdot}7=-1{\cdot}70$.

On increasing P and Q to 1,000 ohms it was found that V should be 0 and $U=505$ ohms for balance (*i.e.*, Brillouin's arrangement). Hence $L/M=-1076/635=-1{\cdot}70$ as before.

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* The numbers were obtained by my colleague, Mr. G. D. West, B.Sc. during the test of a variable mutual inductance of the Rayleigh type.

ABSTRACT.

It is shown that the self-inductance L of a coil of resistance S may be compared with the mutual inductance M between the coil and another by making the first coil one arm of a bridge, $PQRS$, of which the second coil and a resistance $U+V$ in series form one diagonal, the galvanometer forming the other. The cell is connected through a key to the point of contact of U and V. When the steady balance has been obtained U or V can be varied so as to get an induction balance for any value of L/M without P, Q, R or S having to be changed. Then $L/M=-\{Q+S+(1+Q/P)V\}/(T+U)$.

DISCUSSION.

Dr. A. **Russell** said that the author's arrangement was a great improvement on Maxwell's original method. As a student at the Cavendish Laboratory, he had experienced great difficulty with that method. The greatly increased accuracy in inductance measurements due to the use of vibration galvanometers had led to neglect of the older methods, but some of them would be useful in special cases. He asked the author why in his final formula he had made the mutual inductance negative.

Principal **Skinner** said that he had also found difficulty with Maxwell's method, and congratulated Prof. Lees on the simplicity of the apparatus required in his modification.

Mr. W. **Duddell** welcomed an addition to the methods of measuring inductance. The more alternative methods available for checking results the better.

Prof. **Howe** suggested that T and N should be inserted in the figures as well as in the text. He thought Figs. 2 and 3 should be drawn in a similar way to show their close correspondence.

The **President** said that he had always experienced trouble in obtaining a balance with Maxwell's arrangement, and he was relieved to find that similar difficulty had been experienced by workers in the Cavendish Laboratory.

The **Author**, in reply, said he had simply followed Maxwell with regard to the negative sign of the mutual inductance. He would be pleased to make the alterations to Fig. 3 suggested by Prof. Howe.

XI. *An Enclosed Cadmium-Vapour Arc Lamp. By* HENRY J. S. SAND, *Ph.D., D.Sc., Sir John Cass Technical Institute.*

RECEIVED DECEMBER 22, 1915.

THE yellow sodium doublet and the lines emitted by the mercury-vapour arc have hitherto usually been employed in those branches of physical inquiry in which a powerful light of well-defined wave-length was needed. The great importance of having further lines at our disposal, particularly for the measurement of rotatory dispersion, has been emphasised recently by Lowry, to whom we owe the introduction of the mercury arc into polarimetric work; and the use of the cadmium lines was recommended by him.* Lowry describes an arc lamp of the open type in which a cadmium-silver alloy was employed and which thus gave the silver as well as the cadmium lines, and, later, Lowry and Abram give an account of an enclosed cadmium-arc lamp designed to supply the cadmium lines only. In connection with this lamp they express the view that the development of the enclosed cadmium arc promises to inaugurate a new era in the measurement of normal rotatory dispersion, and to effect a revolution in polarimetric methods comparable with that which resulted from the introduction of the mercury arc. The employment of Lowry and Abram's lamp was, however, not very convenient, as it had to be left permanently connected with an air pump. It was started by an electric spark and was run at a low temperature, being water-jacketed, but, even so, its life was not long.

Having been engaged for some years in attempts to construct a cadmium-vapour lamp suitable for more general purposes, I decided to apply the experience gained, to the design of a lamp that would meet the requirements of a laboratory appliance as completely as possible. The lamp which I have constructed for this purpose is run at a fairly high temperature, the metal being melted by means of a Bunsen burner before starting, so that the arc may be struck by tilting; and the temperature of the lamp is maintained high enough to keep the metal in a molten condition and to prevent condensation of metal-vapour on the glass.

The principal difficulties to be overcome consisted in the removal of dissolved gases and oxide from the metal and in preventing it from adhering to the glass, which would lead to fracture of the lamp on heating and cooling. As the lamp is constructed of quartz glass there was also the difficulty of obtaining an efficient vacuum-tight seal for the leading-in wires, but this difficulty was overcome in a perfectly satisfactory manner by the lead-seals described about a year ago.* The oxide and dissolved gases are removed by subjecting the metal to a process of filtration in a vacuum during introduction into the lamp. The adherence to the glass, which would be very great in the case of a metal freed from its coating of solid oxide, is overcome by introducing into the lamp a small amount of a fine powder which spreads itself out over the surface of the metal. The powder chosen for this purpose was always zirconia, obtained by igniting zirconium nitrate.

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* "Phil. Mag.," 1909, 6th series, Vol. XVIII., p. 320. "Trans." Faraday Soc., 1911, 7, p. 267; and "Trans." Faraday Soc., 1914, 10, p. 103.

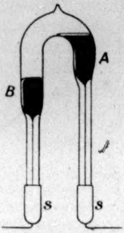

FIG. 1.

Fig. 1 shows the general appearance of the lamp. It will be seen that it consists of a quartz tube bent into an inverted U in such a manner as to give rise to a short cathode chamber A and a long anode chamber B. Each of these chambers is continued in a leg consisting of a thick-walled capillary through which a tungsten wire passes, the lead seals *s*, *s* being fitted at the ends of the legs. Figs. 2 and 2A illustrate the method adopted to fill the lamp. A small amount of ignited zirconia having been introduced at *a*, the lamp is attached to the pump, the piece of cadmium M having previously been placed in a side tube connected with the pump by a tube constricted to capillaries at *b*, *b*, *b* for the purpose of filtering the metal. An alternative plan is shown in Fig. 2A, in which the capillaries are dispensed with and the metal is placed in a cage made of iron wire gauze, by means of which the oxide is filtered off. The quartz glass exit tube to the pump is usually connected to the latter by a ground glass joint disposed at right angles to the plane of the paper, thus allowing the whole lamp to be tilted while evacuated at the pump. After the lamp has been carefully exhausted the metal is melted and allowed to run in.

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* "Proc.," Phys. Soc., 1914, 26, 127.

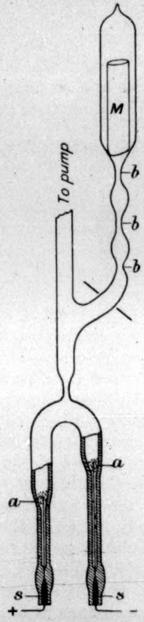


FIG. 2.

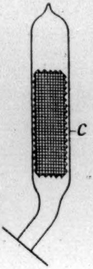


FIG. 2A.

During this process it is freed not only from oxide but also very largely from dissolved gases. If desired, the metal may be further boiled while the lamp is still at the pump. The lamp when drawn off is now ready for use. A convenient plan for setting it up consists in holding one leg in a clamp and taping the insulated leading-in wires and terminals on the shank of the clamp so that they may not be twisted off on tilting. This tilting is effected by rotating the shank of the clamp in its boss head. As already mentioned, the lamp is started by heating with a Bunsen burner from the top until the metal is well molten. When started from the cold it usually lights up even before tilting. It was usually run on a lighting circuit of 100 or 200 volts with a back resistance adjusted to take a current of 5 to 7 amperes on short-circuit. The voltage on the terminals of the lamp is low, usually about 30. Owing to the fact that the small upper chamber holds the cathode, metal distils into it from the hotter lower anode chamber, and drips back again once everytwo or three minutes, causing a slight flicker, which does not, however, interfere with the use of the lamp. It is advisable after use to remove the metal from the bend of the tube, as it would probably otherwise set up strains on solidification which might lead to fracture of the glass. The lamp may be kept burning for an indefinite time; it yields a powerful light, and it is hoped that it maymeet all the requirements of a laboratory appliance for optical purposes.

ABSTRACT.

The lamp shown was similar in general principle to the well-known mercury lamp. It is constructed of quartz glass. To start the lamp the metal is melted by means of a Bunsen burner, and the arc struck by tilting. Before introduction into the lamp the metal is freed from oxide and dissolved gases by a special process of filtration while at the pump. It is prevented from adhering to the glass, which might lead to fracture, by the presence of a small amount of a loose powder in the lamp. The lamp gives a powerful light and once started will continue burning indefinitely.

DISCUSSION.

Dr. J. A. Harker mentioned that when Benoit and Michelson were performing their celebrated experiments on the length of the metre in terms of the wave-length of light it was necessary to make up a large number of cadmium vacuum tubes. One of these only lasted about one day. The light was incomparably poorer than that given by the author's lamp, and the windows were constantly becoming obscured with condensed metal.

Dr. R. S. Willows said he had seen this lamp working satisfactorily for four or five hours on end. For diffraction experiments it was of the greatest importance to have really strong sources of monochromatic light. With suitable filters the cadmium lamp would prove extremely useful for such purposes.

Dr. T. M. Lowry, in a written communication which was read by the secretary, expressed a high opinion of the utility of the cadmium arc lamp. He had used one of Dr. Sand's lamps for over a year, and for laboratory purposes there was no particular in which it could be improved.

Five years of additional experience had confirmed the conclusion which he had come to in 1909, that the best series of lines for exploring all the chief regions of the visible spectrum is obtained by combining the arc spectra of mercury and cadmium with the flame spectra of lithium and sodium. The complete series of lines was as follows : Li, 6708 ; Cd, 6438 ; Na, 5893 ; Hg, $\left.\begin{matrix}5769\\5790\end{matrix}\right\}$; Hg. 5461 ; Cd, 5086; Cd, 4800; Cd, 4678; Hg, 4358. His own experiments on the production of a strong cadmium spectrum had been described elsewhere, and if, as he believed, these had helped to stimulate Dr. Sand in his endeavour to produce a practical arc, their publication had been even more fully justified than he had hoped.

The President asked if the cadmium vapour arc acted as a rectifier in the same way as the mercury arc.

THE GUTHRIE LECTURE.

Some Problems of Living Matter.

By W. B. HARDY, *M.A., Sec. R.S.*

DELIVERED JANUARY 28, 1916.

BEING THE SECOND GUTHRIE LECTURE.

I AM, I understand, to discuss to-day physical problems raised by the study of living matter. There is no lack of such problems. I am embarrassed by their number and variety.

Let me begin by some general account of living matter. A simple single-celled animal of the type of amœba has a volume roughly equal to a sphere of about 30μ radius. It is composed of a translucent turbid material showing no structure. Recently such cells, in spite of their minute size, have been dissected while still living. The operation was carried out under the microscope with fine needles of hard glass, operated by a mechanical device. The result has been to remove some classical misconceptions. One is that living matter has a foam structure. Dissection shows that the appearance of spaces filled with fluid is due to the presence of fat drops, which can be dissected out of the living cell. Such drops are probably merely food reserve, and are external to the living substance. The latter, freed from such masses, is in some places a rigid gel, in others a fluid of high viscosity—that is to say, a slime. Somewhere in the cell is a mass having distinctive properties called the nucleus. It may be either a colloidal solution enclosed in a very tough membrane of transparent gel, or a tough gel containing many granules from $0{\cdot}5\mu$ to $1{\cdot}5\mu$ in diameter, which is rigid in the sense that minute pieces broken off do not round up under the influence of molecular attraction. The living substance is sometimes a puzzling combination of fluidity and elasticity. This is especially the case with the substance of a muscle fibre. A glass needle may be moved about in it in all directions freely, but if a portion be broken off it can be pulled out into a filament of extraordinary length, which when released will almost regain its previous shape.

The ordinary microscope, therefore, teaches us only that the actual living substance when freed from food matters and stored chemical products is a translucent gel or slime. The ultra-microscope carries us a stage further. It shows the translucent material to be composed of an optically homogeneous substance, in which are embedded a multitude of minute particles. Usually the particles are in Brownian movement; the mass, therefore, as a whole is more fluid than solid. But the Brownian movements sometimes cease for a time, to be renewed later. The degree of fluidity, therefore, is variable, the mass, or portions of it, may alter in the direction of a rigid gel, and the change can be reversed. Such a change in the direction of an increase in rigidity seems to entail the expenditure of energy, since it is described as occurring in response to an external stimulus. It is also characteristic of the death change when the free energy of the cell runs down with rise of temperature.

The appearance of minute particles shown by an ultramicroscope is common to colloidal systems, so we may in general regard the living cell as a mixture of colloidal slimes of varying degrees of fluidity. This seems a curiously insufficient basis for the prodigious potentialities of, *e.g.*, an ovum or spermatozoon!

One feature may suggest more to my audience than it does to myself—namely, that though the substance of the living cell is uniformly translucent to light of ordinary wave-length, some parts are remarkably opaque to ultra-violet light. This is true of the nucleus. By taking advantage of this difference, quite sharp photographs have been obtained of the nucleus in the living cell.

The activities of these simplest organisms are at first sight as simple as their structure. Consider, for instance, their mode of progression. It is no more than a flowing of the protoplasm which causes the whole cell to roll along a surface. A few grains of charcoal placed on the upper surface of an amœba are carried forward—*i.e.*, in the direction of motion of the whole animal over the forward edge and backwards along the face in contact with the surface over which it is crawling. It reminds one of Helmholtz's account of the displacement of electricity when a dielectric is rubbed over a surface. The simple movement of an amœba is what would occur if the contact potential difference between the animal and the solid were greater at the front than at the back end.

At intervals the animal takes into its interior particles of food by flowing over them. It dissolves out the portion profitable to itself and extrudes the remnant. But this seemingly purposeful act is very closely copied when drops of chloroform in water are fed with particles of glass coated with shellac. The particles are pulled into the interior of the drops, the shellac dissolved and the indigestible masses of glass thrust out.

We have merely to observe the marvellous variety of animal and plant life to realise that this appearance of simplicity must cover a real complexity. The appearance of simplicity is, indeed, but an example of the characteristic of living matter, the adaptation of the means to the end. The phenomena are simple only so long as the object to be attained is simple. Take movement as an example. I have watched one of these simple cells endeavouring to bend and break a chain of bacteria so as to get short lengths capable of being ingested. During the operation a particular cell became extended between the ends of a chain until it had the form of a cylinder about 30μ long. The movements now took on an entirely different character. The cylinder swelled out at one end, and the swelling progressed as a slow wave forward and backward over the length of the cylinder. Simple flowing movements were replaced by an orderly rhythm of waves of shortening.

Let us take another illustration. Some animals of the simple type we are considering get their living as the spider does, by spreading a net. The net has not the geometrical regularity of those which are hung in the hedgerows where they condense the atmospheric water to such delightful patterns, but not the less are they nets spread to catch prey. The threads are actual processes of the body of the animal—the pseudopodia of the zoologist—and each single thread is a cylinder only a few μ in diameter. Such a cylinder considered as a figure of tension must be highly unstable. The tension of the surface probably is small compared with that of water. Certain evidence would fix it about 45 dynes. The maintenance of this thread of semi-fluid material, therefore, either is due to a solidification of its surface or needs continuous expenditure of energy. The matter does not end here however, for the thread is not a simple cylinder of protoplasm. The substance is in movement; the motion of the minute particles floating in it show that there is an outward and an inward stream or flow, and at the face where the two streams meet the frictional stresses produce double refraction.

Consider also the puzzling discriminations exercised by the surface of these simplest cells. When two parts of the same animal come into contact the surfaces soften and the parts fuse, but this does not occur when different individuals touch.

The living cell is, in fact, a machine, capable of carrying out movements, and of complex growth and differentiation of substance. Oxidative processes are the source of its energy, but the oxidation is not direct, as in the burning of a candle. There is a store of energy which is set free in response to a stimulus, and the intake of oxygen occurs only *afterwards*. The oxygen *restores* the potential. A large variety of ferments are present either actually or potentially. They are set free, and can be identified when the cell is broken down and its material dissolved.

Now, living matter contains from 80 to 90 per cent. of water. In any ordinary dead gel or slime with so much water, diffusion would obliterate differences of state so far as simple chemical substances such as salts are concerned. Initial differences in the state of aggregation of the colloid would not so readily disappear owing to the slow rate of diffusion, but if electrolytes were present they would, by their diffusibility and profound influence upon colloid structure, tend to produce a uniformity. Living matter is remarkable in the fact that we have freedom of interchange of matter, otherwise nutrition would fail, combined with the preservation of sources and sinks of energy in a material which is essentially a fluid.

The most fundamental, and to my mind the most puzzling, problem of living matter lies in this contradiction between the functional and chemical complexity of living matter and the apparent simplicity of its structure. Both microscope and ultra-microscope tell us simply that it is a colloidal sol of high but varying viscosity. The material basis of life is apparently much less structural than, for instance, a simple gel such as, *e.q.*, that of azomethine. This is at first sight merely a translucent yellow glass, but the microscope shows it to be a weld of masses, each of independent origin; each of these masses is a weld of smaller masses arranged in an orderly pattern, and these again are built of ultra-microscopic particles.

The questions which I specially wish to discuss are raised most directly by the phenomena of growth. The growth of living matter has been compared to many things—to the growth of a crystal, among others. In the growth of a crystal, molecules of the same nature as those which constitute the crystal are aggregated to a definite formal pattern. In the growth of living matter, extraneous molecules also are ordered to a particular pattern, but the molecules are not the same as those which constitute the growing mass. Growth is part of a cycle of chemical and physical changes. The case of the crystal is helpful as furnishing an example of the directive influence of a pre-existent molecular pattern. Perhaps it is not generally known that similar directive action is manifested by dead colloids. Many colloids are systems following a path of change whose form is determined by their previous history. The course of the change with time and at constant temperature of the viscosity of, for instance, a solution of gelatine is determined by the temperature at which the solution was made and by the rate of cooling. If, now, this solution is sown with small portions of another system, say with bits of gel, the path of change is altered completely.

We thus have analogies in the world of dead matter for individuality in the characteristic path of change of colloidal systems, and for the directive influence which underlies growth in both crystals and colloids; but a remarkable feature of living matter is the distance over which such directive influence appears to be exerted. The regeneration of cut nerves perhaps best illustrates this.

Let me first premise that the growth of any part of a cell is controlled in some unknown way by the nucleus. When individuals of the single celled type are cut into pieces most of the fragments grow and regenerate the entire animal; but this power of regenerative growth is limited strictly to those fragments which contain a portion of the nucleus.

Consider now a nerve cell and its related nerve fibre. The latter is a process which grows out from the former, and is covered by certain insulating sheaths. The cell body containing the nucleus varies much in size, but we may put it as roughly equal in volume to a sphere of 50μ to 100μ in diameter. The cell process or axon divested of its insulating sheaths is a delicate rod of protoplasm, 5μ to 10μ in diameter, which, in a large animal such as a whale, may be some metres in length. The integrity and the power of growth of the whole of the axon is dependent upon the nucleus. If the nucleus is destroyed the whole structure perishes, and if the nerve fibre is cut that portion of the axon which is still in connection with the nucleus grows, whilst the part cut off disintegrates and dissolves. The nerve fibre, therefore, furnishes us with an example of a system capable of growth only so long as it is united with a portion of matter, which may be some metres distant and to which it is connected only by a cylinder a few μ in diameter. I do not think that there can be any transport of actual nutritive material by such a tenuous connecting link. The relation may be a static one, the molecular pattern of the nerve fibre being unstable when isolated from the nerve cell. But such scanty evidence as is available tends to show that it is a dynamic one in the sense that the integrity of the molecular structure of the entire axon is maintained by expenditure of energy. The nucleus and cell body, in upholding the molecular pattern, may be said to exert a directive influence along the whole length of the nerve fibre.

The immediate environment of the growing face of a cut nerve fibre also exerts a remarkable directive influence upon its growth. It must be known to all of you that the severed ends of a nerve will heal so as to give complete restoration of function. The nerve in question may be a bundle of some thousand fibres, along which the nervous impulses which produce the exactly controlled movements of skilled action are transmitted, and the restoration of complete function after section is like the joining together of a bundle of cut telephone wires in such a way as to restore all the connections.

For complete restoration of function it is not necessary to fit the cut ends of the nerves closely together. They may be left in the wound separated by a space of some centimetres. Imagine them so separated. From the central end—that is to say the one whose fibres are still connected with the nerve cells—the axons grow out. The axons of the peripheral end break up and dissolve. Now the growth of the axons is at first aimless in direction, the filaments making their way along lines of least resistance in the spaces of the tissues. After a time, however, they come under some influence emanating from the other cut end of the nerve. They turn and grow as directly as possible towards it, and finally invade the empty sheathes and grow down them. What is the nature of the directive influence? It is without doubt chemical. Some substance diffusing out determines the direction of growth, for when two tiny tubes of celloidin are placed near the cut end, one filled with an emulsion of liver and the other with an emulsion of nerve, the axon filaments grow towards the latter. They are, as it were, attracted by it.

The direction of growth must be determined by the density of a diffusion column. If we take the end of a single axon as the end of a cylinder 5μ in diameter, and if it is inclined at a small angle to the axis of diffusion, the difference in the rate of growth of different parts of the cylinder needed to orient it must be produced by differences in the concentration of the diffusing substances which occur in distances less than 1μ, measured along the axis of diffusion. I need not emphasise how minute these differences must be.

It looks as though we might have to claim for the axon the perfect sense of direction ascribed by a student to amœba. Asked to describe the response of this animal to an electric current, he said : "When subjected to electricity an amœba withdraws all its pseudopodia except one, and then directs itself to the North Pole ! "

Let us consider the directive influence which underlies growth from another point of view. The complex organisation of the higher animals exhibits well-marked periods of growth, decay and death, and the duration of these periods is characteristic of each species—the three score years and ten of man, for instance. But these periods are not obvious in the history of single-cell types, in which the whole cell simply divides to form a new generation. Indeed, the question arises whether decay and death are intrinsic properties of these animals. Individuals of the species Paramœcium have been isolated under normal and healthy conditions. Each individual was the starting point of a series of generations, there being on the average two generations in three days, and the rate of division was recorded, the records furnishing the basis for a curve of vitality. Such a curve shows fluctuations of a fairly regular character—"rhythms," they have been called. The curve alternately rises and falls, and each complete rhythm, a rise and a fall that is, lasts about a month. The curve as a whole, however, was found steadily to fall, until at about the hundred-and-seventieth generation the race dies out. This was held to establish the appearance of senile decay in strains isolated from mixture with other strains but otherwise in completely healthy surroundings. The discovery that unfertilised eggs of sea-urchins could be made to develop by immersing them for a few hours in more concentrated sea water suggested the possibility that senility could be cured in protozoa. Therefore, when the period of decay had arrived, and individuals were dying off rapidly, the effect of placing the individuals in various infusions was tried. The infusions of animal tissues were found to give the required result. After exposure to them for a short time the rate of growth and of reproduction reached the normal level, death ceased, and a strain was maintained in full vigour for 860 generations. The living matter of these cells seems to be potentially immortal.

The point of immediate interest in these experiments is that, in the periods of depressed vitality, the power of heredity in determining form becomes imperfect, and many "monsters" are produced. We have here, then, a wearing out of the directive influence which underlies growth.

In the process of artificial rejuvenescence it cannot be a chemical insufficiency which is made good; it must be a physical state which is restored. This is obvious when we consider a special case. Thirty minutes' immersion of an individual paramecium in 0·1 per cent. potassium phosphate was found to restore vitality, and the effect persisted for 282 generations. The effect cannot be due to the presence in individuals of a trace of the salt, for each generation would halve the amount, so that as early as the twentieth generation less than a millionth part would be left for each individual.

It will be remembered that when a solid surface has been washed by a salt solution the contact potential of the surface with pure water is altered, and, according to Perrin, simple washing with water fails to restore the original state. It is, I expect, the wearing out of this kind of state which leads to senility.

Recent work on nutrition suggests reconsideration of these experiments on protozoa. A diet must, of course, contain water and a supply of fuel in the shape of proteins, fats and carbohydrates. It must also contain substances which do not contribute energy, such as simple salts and a class of substances whose presence has only been recently detected called vitamines. Nothing is known of the chemical nature of these substances nor how they act, but incredibly minute quantities are sufficient.

The existence of and need for vitamines first appeared, I believe, in connection with the disease beriberi. This is a disease of the nerves, and it was noticed that birds fed on polished rice—that is to say, upon rice free from its pericarp—developed beriberi, but recovered if the polishings themselves, or an alcoholic extract of the polishings, was added to the white rice.

Once attention was drawn to these accessory foodstuffs instances of their occurrence multiplied quickly. They have been found necessary for mammals, birds and minute plants. Scurvy seems to be due to their absence from preserved foods.

Their influence would appear to be limited to the processes underlying growth. The following two cases illustrate this and also indicate the minute quantities necessary. When young rats are fed upon artificial milk made by mixing together in the right proportions the component substances of ordinary milk, previously separated and purified, they lose weight and die. Now, to convert artificial milk into a perfectly adequate foodstuff all that is needed is the addition of 2 per cent. of ordinary milk. Certain Continental workers challenged this result, but later they had to confess their error, which arose in an interesting way. The commercial pure lactose which they had used to make the artificial milk was found to contain vitamines. Even after four re-crystallisations two grams a day carried enough vitamine for a 50 gram rat. Only by many re-crystallisations is vitamine free lactose produced.

Another case. The common brown diatom of the sea litoral will not grow at all in artificial sea water, but will grow very freely in such water to which as little as 0·2 per cent. of natural sea water has been added.

The intimate connection between vitamine and growth is illustrated by the case of cancerous tumours. Mice can be kept at constant weight on a diet of purified wheat protein, starch, lard, lactose, salts and water. Some mice, previously inoculated with a rapidly growing sarcoma, were put on the artificial diet, others similarly inoculated upon a normal diet of bread and corn. The cancer was found to grow much more slowly in those on the artificial diet. To give an example, a mouse after 52 days of artificial diet showed a tumour only 4 mm. in diameter. It was then put upon normal diet, with the result that in 30 days the tumour was nearly as large as the mouse itself. Too much must not be based upon this result, interesting as it undoubtedly is, until it is fully confirmed.

It has been suggested that vitamines intervene in growth by contributing to the fixation of the molecular pattern of the newly formed substance. Their action has been compared to that, say, of a dextrorotary crystal which by its presence causes a mass of fluid indefinitely larger than itself to deposit right-handed crystals. The analogy can at the best be but rough. The influence of a crystal is limited to directing the system along alternative paths of change, all of which increase the entropy. In the growth of living matter, however, the local change, at any rate, is from simple to complex, from a lower to a higher content of free energy.

The nerve fibre of an adult animal grows only when it is cut. The faculty is latent in the completely functional structures; therefore, though growth and function affect each other, they must be distinct process in the sense that the whole cycle of change of energy and matter which constitutes function may occur without growth. If vitamines intervene in growth by a stereochemical effect upon the construction of new matter, the other class of accessory foodstuffs—namely, the simple salts—stand in interesting contrast, since they exert a directive influence chiefly upon the changes of energy which constitute function. The amplitude, period and form of the contraction wave of the heart are, for instance determined by the nature of the electrolytes present. The rhythm of the heart muscle appears to be based upon the antagonistic action of univalent and bivalent cations. The voluntary muscles have no intrinsic power of rhythmic movement. They respond only to the nervous impulse or to some external stimulus. But one of these muscles immersed in a bath of the right kind and concentration of electrolytes, will beat as regularly as the heart itself. The regulation of respiration—that is to say, the adjustment of the rate and depth of breathing to the needs of the body—also is based upon the extreme sensitiveness of a portion of the brain to variations in the hydrogen-ions concentration in the blood. Normally this has the value $10^{-7.3}$. Scrambling up a mountain 1,000 ft. ascent in 30 minutes alters this only to $10^{-7.1}$.

The physical basis of this hold which electrolytes have on the activities of living matter is clear. The configuration of a colloid is determined as much by the electrolytes present as by its own chemical nature. The inertia of a colloid—that is to say, the degree of resistance it offers to change—is determined by electrolytes, since they provide what Helmholtz calls the "first condition of electrical distribution," as between the colloid particles. It is possible by eliminating electrolytes to raise the sensitiveness of some colloidal solutions to the point at which they are stable in quartz vessels, but are at once precipitated when transferred to clean glass vessels.

Exposure to distilled water also increases the sensitiveness of the surface of some living cells without destroying it. They will live and thrive in pure distilled water, but a trace of metallic impurity (estimated at 1 in 70,000,000) will quickly destroy them.

Here, I think, a certain broad conclusion is forced upon us. Since electrolytes control the configuration of colloidal systems in respect to the size, number and distribution of the colloid particles, and also shape the path of change of energy in living matter, we may infer that the functional processes of a cell are conditioned by the configuration of the colloid in the sense mentioned above.

The material which manifests the phenomena of life is, as I have said before, nothing more than an optically homogeneous fluid medium, in which are suspended particles. When the store of potential energy is being drawn upon—that is to say, in the functional state of activity—the fluidity is decreased and a transitory stage of gelation may occur. Thus, when the cell substance contracts under stimulation, and in the death change when the potential energy is dissipated as heat fluidity decreases to the point at which Brownian movement of the particles is suppressed.

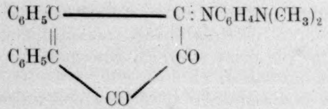
Also the establishment of the field of force which brings about division of cells in the process of multiplication is accompanied by a local gelation.

What physical significance can be attached to this decrease in fluidity ? According to the theories of Einstein and Hatschek a decrease in the fluidity is due to an increase in the volume of the colloid particles following upon an intake of water from the continuous medium. I do not think so simple a theory covers the facts. Their formula fails except in the case of the simplest hydrosols and suspensions. Actual observation of the process of gelation under the microscope reveals only an inconsiderable change in volume. The main events seem to be, firstly, a damping down of the Brownian movements ; and, secondly, an agglutination of the particles into rows which form the fibres of a quasi-rigid framework.

It is practically certain that the process does not go so far as this in normal functional states. The colloid particles maintain their independence, but their relation to each other and to the continuous medium are changed in such a way as to make their potential energy a function of their position. The molecular mechanism of these changes is quite obscure. We may picture to ourselves the colloid particles as strain centres—the microscope justifies so much—and the continuous medium as having the mechanical properties of an unannealed glass. Mechanically a living cell has many points of similarity to a Rupert's drop ; indeed, many forms violently disrupt if the surface "skin" is cut through. Unfortunately we do not know the basis of the simple rigidity of glasses. The absence of any discontinuity in the change from fluid to glass similar to the discontinuity of energy and property which marks the change from fluid to crystal shows that a glass is a fluid which has lost its characteristic property of fluidity, but to the question why the molecules lose their freedom of movement there is at present absolutely no answer.

One fact may be seized upon—namely, that a change from fluid to a solid of the gel or glass type may be due to quite a small local change in a complex molecule.

Consider, for instance, the substance azomethine, which has the formula :—



This substance has the property of forming rigid gels with *any* solvent; with ether, alcohol, benzene, chloroform, &c. But these very exceptional colloidal properties totally disappear if one hydrogen atom of the side chain is replaced by bromine. I think we are here in a region of molecular physics which is practically unexplored.

The damping of Brownian movements in the course of the functional activity of living matter is, I think, a clue of the first importance to the mechanics of the cell. It suggests a much more extended "grip" of the colloid particle upon the continuous medium than would be indicated by current conceptions of the range of molecular action.

There are properties of simple hydrosols and of suspensions of living cells which point in the same direction. The simplest hydrosols, for instance, seem to have saturation points; that is to say, the number of colloid particles in a cubic millimetre cannot be increased beyond a certain point without occasioning precipitation, and the saturation point seems to be reached when the particles are still widely separated. A similar relation appears in a much more complex system—namely, a suspension of bacteria in a nutritive medium. As the bacteria grow and divide, the rate of growth slackens and finally ceases, but this is not due to exhaustion of the medium, for if the bacteria are filtered or centrifuged off, and the material freshly inoculated, a fresh and copious growth results.

Very little is known about these curious saturation points, but I think you will agree that what is known suggests a range of influence of one particle upon another much greater than the range ascribed to molecular action. Something of the same kind is seen in thin sheets of fluid. A layer of carbon tetrachloride on water exhibits curious mechanical instabilities even when it is of the order of a millimetre in thickness. Such a sheet of liquid is like an unannealed colloid. The tension of the upper face, the air face, is 24 dynes, whilst that of the water face is 50 dynes, and I think there is much to be said in favour of the view that these unequal stresses make themselves felt throughout the entire thickness of the sheet.

I am inclined to suggest the phrase "range of molecular action" must be held to refer to two distinct things—the one is the range of an isolated molecule, say, a molecule of a gas in its free path; the other is the orienting influence of molecules upon one another in the close packed states of fluid, glass, or gel.

The true range of molecular action is that of the gas molecule. It is probably very small, of the order of 10^{-8} cm. But in the close packed states it is probable that the asymmetrical field of force at an interface produces distortion of the external fields of the molecules and orientation extending on either side until it is upset by the heat motion. On this view the transition layer at an interface is a region of more or less fixed molecular pattern, akin, perhaps, to that of a glass. Before the war I had begun to observe particles of interfaces under the ultramicroscope with the object of detecting signs of such structure. It is certain that the Brownian movements are sometimes damped in a remarkable way in this region. The depth of these transition layers might be expected to be increased when the molecules involved are large, or, if small, when the external field of each molecule is markedly asymmetric about the centre of mass. It is significant that the influence of electrolytes upon living matter and upon complex organic colloids with large chemical molecules such as proteins, is determined by the volume of the ion as well as by the charge

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* The evidence however is not wholly one-sided. In Einstein and Hatschek's formula for the viscosity of two-phase systems the viscosity is given as a simple fraction of the ratio between the volume of the dispersed phase and the total volume. When the degree of dispersion is high so that the particles of the one phase are ultramicroscopic the viscosity is greater than would be given by the formula. If, now, it is assumed that the discrepancy is due to the volume of the dispersed phase being increased by what might be called adsorption envelopes, it is found that these latter need be only 0·87 μ in thickness. But the formula also fails in other respects.

carried; whereas the effect upon simple interfaces between fluid and solid and upon simple suspensions and hydrosols is determined solely by the charge.

Mere increase in size of the molecule must of itself introduce new considerations into molecular physics. The molecular weight of the red pigment of blood, itself a complex protein, is about 16,000; its volume would be equal to some hundred water molecules. The energy related to it when in solution will be its own kinetic energy, and the surface energy of the water molecules surrounding it. Also if it is to be regarded as an elastic structure there will be potential energy due to bulk compression produced by the intrinsic pressure of the fluid.

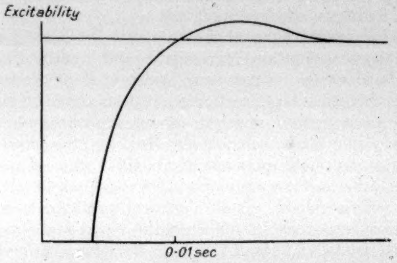
We are compelled, I think, to attribute surface energy to these large molecules, not, of course, strictly to the molecule itself, but to the displaced water, by the fact that they are aggregated by minute traces of electrolytes in a way resembling the effect upon coarse colloid systems and suspensions. A molecular solution of hæmoglobin is possible only in very pure water.

It is curious that large molecules sometimes exhibit simple physical relations. Most proteins obstinately refuse to form states simpler than complex solutions or complex slimes or gels. Some, and hæmoglobin is one of these, readily crystallise. Now hæmoglobin when it crystallises preserves its peculiar optical characters unaltered. It has the same colours and the same absorption bands. It also continues to manifest the same special relations to gases as it has when in solution. Essentially it is unchanged. This continuity of physical properties exhibited by so large a molecule is, I think, startling when considered in relation to Prof. Bragg's account of the structure of crystals.

I have no time to deal with the changes of energy in living matter. The subject is too complex for brief treatment, but I should like to offer a special problem. In general the energy changes of the living cell manifest the ordinary features; they are, for instance, accompanied by the dissipation of a fraction of the energy on heat. One case, however, presents puzzling features—that of the nervous impulse. This is a short wave of molecular change which progresses along the axon filament at about 30 metres a second. It can be started by a local chemical, electrical, or mechanical change. The passage of the wave over any region is followed by a brief period of complete inexcitability, followed by rapid recovery of function. The molecular change involved in the wave is, therefore, one which needs a finite, though very short, time to be recovered from. One would conclude that the wave is a discharge of energy which has to be made good before another discharge can take place.

This conclusion is borne out by the fact that recovery of function can occur only in presence of oxygen, and also by the fact that if the wave passes through a region in which its amplitude is diminished by cold or narcotics it is restored to its full extent so soon as it emerges into a normal region.

The wave would, therefore, appear to be one of chemical change, but if this be so it is one of exceptional character. The temperature coefficient is very low for a chemical change, being only 1·78 per 10 deg., and there appears to be absolutely no concomitant liberation of heat. The absence of any heat change is, however, I suppose, no more remarkable than the limitation of the rays emitted by phosphorescent animals to visual rays, and the energy of these rays is certainly due to oxidation.



Curve showing Recovery of Excitability in a Nerve after Activity.

The profound difference between living matter and a simple gel is seen in the selective permeability of the former. Selective absorption of dyes is a common property of gels. Thus, gelatine gels condense basic dyes more than acid dyes. Gels of agar condense acid dyes more than basic dyes. But the permeability of living matter is both curiously selective and variable. The act of fertilisation of the ovum—the entry of the spermatozoon, that is—is followed by a passing rise in the permeability of the surface. In some cases permeability is said to be unidirectional. When the living skin of the frog is used as an osmometer membrane it is said to permit the passage of carbonic acid in only one direction—namely, from its internal to its external surface. Permeability has been most completely studied in the kidney, and it appears that selective permeability is controlled by or due to an expenditure of energy by the living membranes of the kidney tubules.

The business of the kidney is to maintain the blood of a certain normal composition as regards certain constituents. For our purpose we may regard the blood as a solution of certain colloids—mainly proteins—and of other solutes of simpler molecular character such as urea and salts. The kidney also appears to be chiefly responsible for maintaining the proper reaction of the blood—that is to say, the normal ratio of hydrogen and hydroxyl ions.

Consider first the removal of excess water. This is governed by simple considerations of osmotic and hydrostatic pressure. Incidentally we get clear evidence, if physicists were in need of it, that large molecules, such as those of proteins, exert osmotic pressure. In an osmometer whose membrane is freely permeable by salts, sugar, urea, &c., the blood shows a permanent osmotic pressure of about 35 mm. of mercury. This is the osmotic pressure of what we will call for short the colloids of the blood. It is a critical pressure as regards the elimination of water, for when the blood pressure in the renal arteries falls to about this level the flow of urine ceases, because the hydrostatic pressure of the blood is then equal to the opposing osmotic pressure.

Now there is a certain solution of salts called Ringer's fluid, much in use in biological investigations, which represents very closely the salts of the normal fluids of the body. If some of this solution be injected into the blood there is an immediate flow of urine which is just the Ringer's fluid, or its osmotic equivalent, which has been added. The cause of the flow is obvious. The added Ringer dilutes the blood colloids and lowers the osmotic pressure. The result is that the balance between osmotic pressure and the hydrostatic pressure of the blood is upset and fluid flows out.

That the kidney plays a passive part is proved by the fact that in such a case a copious flow of urine occurs without any increase in the rate of oxidation in the organ. There is thus no expenditure of energy in the process.

That the colloids of the blood plasma exert their influence simply in virtue of their osmotic pressure, and not because of their chemical nature, is proved by the fact that if gelatine be added to the Ringer's fluid in quantity sufficient to give the osmotic pressure of the blood colloids and the fluid injected there is no diuresis. But if soluble starch be added until the viscosity of the Ringer's fluid is, say, twice that of blood (3 per cent. starch), the diuresis is much the same as with simple Ringer's fluid. This is because starch does not sensibly increase the osmotic pressure of Ringer's fluid.

But a flow of urine may be provoked by the injection of alkaloids or of urea or of a simple salt such as sodium sulphate. Consider the case of sodium sulphate. The injection of this salt essentially alters the chemical character of the blood. A diuresis is at once set up and a urine rich in sodium sulphate eliminated. In this case the living membrane discriminates in a remarkable way between sodium sulphate and the normal salts of the blood. That is the usual way in which the physiologist puts it, but it is as well to remember that the discrimination may be due to the remarkable colloid complex which is present in blood plasma. At any rate, be that as it may, a differential treatment is accorded to the sodium sulphate or to, for instance, urea. Such selective diuresis is accomplished only at the expenditure of energy, as appears from the increased intake of oxygen by the organ. The physical processes underlying the transference of solutes or water in the body are probably very complex. For simple transference of fluid through a membrane one's mind turns at once to electric endosmose. When a current is passed through a rod of gel there is an endosmotic movement of water, due to the fact that the colloid particles are usually at a different potential to the fluid bathing them. We may conjecture, therefore, that an electrostatic field maintained across a living membrane would cause transference of fluid. When an expenditure of energy takes place in living matter its potential rises above that of the neighbouring inactive medium. For instance, the contracting portion of a muscle fibre, or the part of a nerve fibre actually conveying a nervous impulse, show a raised potential. Also, when a flow of saliva is excited, the electrical potential of the gland as a whole is altered. There can, therefore, be no question of the ability of a living membrane to produce a difference of potential between its two faces. But in simple electric endosmose the transport of fluid is due to an external field acting upon that portion of the fluid which is charged, owing to contact with the containing walls. In the living gland there is nothing to take the place of this external field. If a difference of potential is established between he two sides of the living membrane, it is due to a change in the colloid walls themselves.

Suppose a gradient of contact potential were maintained along the length of a tube holding fluid, would a flow of fluid result? I am inclined to think it would, the necessary flux of electricity taking place through the fluid or through the walls.

The transference of fluid in a living cell, instead of being a simple endosmotic phenomenon, is most probably based upon variations in the water-holding power of colloid systems in different states. The imbibition of fluid by a body such as gelatine is a very obscure phenomenon partaking of the character of solution and of endosmotic movement. Whatever its origin, the water-holding power is easily altered. Exposure to the vapour of formaline will completely change the character of the gel. Its structure changes, the gelatine is altered so that it ceases to be soluble in water, and, though there is no immediate change in volume, the gel which has been "coagulated" by the formaline has its vapour pressure raised. It holds water much less firmly. The partial coagulation which occurs in some processes of life, the change from a slime to a rigid gel, for instance, are unquestionably accompanied by variations in the potential, in Gibb's sense, of the water. If the surface film of a colloid membrane separating two masses of fluid were to change in such a way as to lower the potential of the water in it, water would enter the region from both sides simply. But if the change of state were to be propagated as a wave of change starting at one face and dying out at the other face, water would be carried along from the one side of the membrane to the other. A succession of such waves would maintain a flow of fluid.

I should like, in conclusion, to say a word as to the physical knowledge which the biologist is now in need of. The biologist has to deal with the molecular mechanics of gels and slimes. When the formation of a gel is followed by the microscope or the ultra-microscope, the change of state is seen to be due to an increase in size of the colloid particles, followed by their coalescence to form the fibres of a sponge. The fibres of the sponge, in many cases at any rate, are amorphous solids, like a glass. Now we know that there is no break between the state of fluid and that of glass or gel such as there is between fluid and crystal. Even viscosity shows no discontinuity. Generally speaking, all physical properties pass over without interruption from the one state to the other. A gel or a glass, therefore, is in this sense a fluid which has lost the characteristic property of fluidity. What the biologist first of all wants to know, then, is the molecular mechanism of this change. When a fluid becomes a glass the fields of force about the molecules, as I picture it, become interlocked, so that, although the crystal state is not reached, the potential energy of a molecule in the interior of the mass ceases to be independent of its position. Osborne Reynold's work upon dilatation is helpful in this connection, but I do not think it carries us far.

To understand the gel or slime it is first necessary to understand the fluid state, and, unfortunately, though physics has much to say of the molecular structure of gases and crystals, that of fluids is still very obscure.

Colloidal systems frequently are systems undergoing spontaneous change. As Graham said, they contain "inergia." But in a dead colloid the "inergia" is due to differences of concentration which right themselves slowly owing to the slow rate of diffusion of the solute and to delays caused by internal surfaces. The remarkable hysteresis of surface films similarly springs from the slowness of tangential diffusion, as Gibbs pointed out. The available energy of a dead colloid or of an interface is in the main physical in character. That of living matter is essentially a chemical potential, and the chemical potential gives way in the response to a stimulus, and is restored by an intake of oxygen. The activities of a living cell appear to be due to a cunning combination of the chemistry of the dead space with the hysteresis of the colloid. The well-known drop of mercury in a very dilute acid solution of a chromate might perhaps be taken as a model. The drop is thrown into regular pulsation by intermittent contact with a wire. But the drop of mercury must be reduced in size until the chemistry of its surface becomes a rapidly varying function of its radius, such that if a displacement occurs a train of pulsations results.

ABSTRACT.

The lecture dealt with the physical aspect of some of the phenomena of living matter. At the outset some of the snares and pitfalls which beset the path of the physiologist in search of physical

facts were indicated. One of these was the effect of instinct or intelligence in anticipating altered circumstances, and in setting the appropriate physiological process in action even before the actual change in circumstance had taken place. For example, in some experiments to determine the time lag of increased respiration, it was found that the subject—a cyclist—always anticipated the application of the load and the acceleration of his breathing commenced *before* the actual increase in effort of which it should be the consequence. Then, again, many of the long-accepted theories of the structure of living organisms were ultimately found to be due wholly to the method of killing the organism and preparing it for examination. Exactly similar structures could be obtained in pieces of gelatine if treated in the same way.

Many phenomena were quoted to illustrate the close analogy of many of the functions of living matter to processes familiar to the physicist and physico-chemist. In some of these—for example, the digestive processes of certain organisms—the analogy was so complete that the whole process could be reproduced exactly with non-living material.

The principles underlying growth and development were outlined, and it was shown that growth depended on the presence in the food of *vitamines*. Thus, in the case of white mice fed on artificial milk made by mixing together the purified constituents of ordinary milk, but containing no vitamines, growth ceased altogether, while if 2 per cent. of ordinary milk were added to the artificial milk the growth rapidly became normal. Another example of the influence of these vitamines was that, in pure distilled water, it was impossible to obtain a development of living organisms, but if the slightest trace of tap water were added—putting a stopper in the bottle which had previously been in a bottle of tap water was sufficient—the organisms would thrive quite normally. The fact that such small proportions of nutriment containing vitamines was sufficient suggested a parallel between their action and that of a few crystals thrown into a supersaturated solution of a salt in initiating a crystallisation of the whole.

A further example of the subtle influence of physical laws in physiological phenomena was contained in the explanation of the joining up of severed nerve processes. The directive action involved in this was stated to depend on extremely minute concentration gradients.

Many other interesting phenomena were described and explained.

XII. *Experiments on the Flow of Heat in Metal Sheets.* By

SIDNEY SKINNER, *M.A., Principal of the South Western Polytechnic Institute, Chelsea.*

RECEIVED MARCH 7, 1916.

A METHOD of showing to a class the conductivity of heat along a bar is to place the bar under a specially prepared paper which changes colour with heat. The experiment is not satisfactory, because paper is too poor a conductor, and the colour effect has no definite edge. I attempted to find a remedy for the poorness of conductivity by backing the paper with a metal plate. This, although it showed in a general way the flow from a tongue of metal into a sheet, was still not satisfactory on account of the indefiniteness of the colour effects. The metal plate used was cut from a sheet of tinned iron, and I noticed that the edge of the region where the tin had melted could be seen very definitely. The tin melts with a sharp edge which forms an isothermal or equi-temperature line corresponding to its melting point—227°C. Inside this sharp line other equi-temperature regions are shown by the oxidation colours of tin. Each oxidation colour seems to correspond to a definite temperature. When the melted tin solidified the crystals arranged themselves differently to the arrangement in the original plate, and the equi-temperature line may be very sharply developed

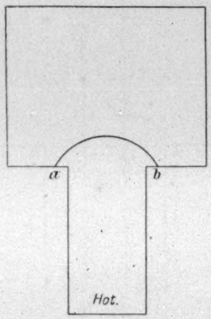


FIG. 1.
ab is the curve of melted tin.

by washing the surface with a mixture of bleaching powder and hydrochloric acid. I have used this plan of observing the line of melting on the surface of tinned iron to examine the flow of heat in iron sheets cut in different shapes with a view of comparing the equi-temperature lines with what would be the equi-potential lines in current flow through similarly shaped sheets. This method of demonstrating the equi-temperature lines is similar to that used by de Sénarmont, "Ann. Chim. Phys.," 21, 457, 1847, who used a wax coating, and to that used by other experimenters including Voigt, "Wied. Ann.," 60, 350, 1897, who used elaidic acid mixed with wax and turpentine.

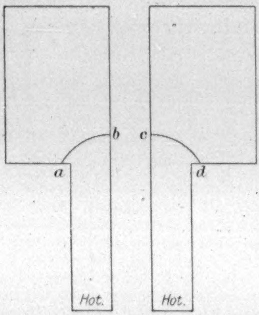


FIG. 2.

ab, *cd* are the curves of melted tin.

One problem examined was the flow of heat from a tongue into a large sheet. The sheet was placed on a tile or piece of asbestos, and the tongue was heated by a bunsen flame. As the heat proceeded into the sheet the melting of the tin could be watched, and it was noticed that the edge of the melted tin took the shape of an ellipse, with the minor axis in the direction of the tongue. This is illustrated in Fig. 1.

We may compare this with the flow of electricity from a tongue into a plate. Equi-potential lines take the same form as the equi-temperature lines.

It is an electrical law that if a plate be cut along a line of flow no change will take place in the equi-potential lines in the portions which are formed by the cut. I have made a similar experiment with the flow of heat in a tinned sheet by cutting along the tongue and through the sheet in the direction of flow. In the two portions I have studied the flow of heat separately. On putting them together the equi-temperature line was the same as in the uncut sheet. This is illustrated in Fig. 2.

With these results should be compared the equi-potentials as calculated and mapped experimentally by Prof. C. H. Lees, "Proc." Physical Society of London, XXI., 309, 1909.

Another problem I have examined is the flow of heat into a circular disc and out from a circular disc. A piece of tinned iron is taken, and the circular disc cut from it with two tongues to it, one for the source of heat, and the other for the sink. When this is heated an equi-temperature line exactly analogous to the equi-potential line in current flow may be observed. By taking a number of similar sheets, equi-temperature lines corresponding to different extents of flow may be obtained. Where the heat enters the equi-temperature line is concave to the entrance, and where the heat leaves the line is convex to the entrance. These results are illustrated by diagrams, Fig. 3, and

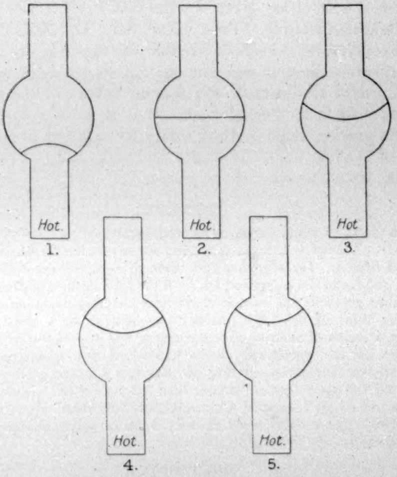


FIG. 3.—VARIOUS STAGES OF FLOW.

if a number of these diagrams are prepared and placed in a thaumatrope the flow of the heat in and out may be demonstrated.

Various shaped plates have been cut out and examined. Among these I may mention an L-shaped plate to show the flow round the right angles ; a plate with a narrow neck in it ; a plate cut in the form of a section of an air-cooled engine to show the influence of the ribs on the outer wall of the engine.

The similarity between the equi-temperature and the equipotential in current flow is well shown by comparing the figures obtained with those given by the late Prof. Grylls Adams in his Bakerian lecture, " Proc." Roy. Soc., Vol. XXIV., 1875.

In conclusion, I desire to say that the experiments have been described because it was felt that other teachers would find them useful to illustrate the general nature of the equi-temperature lines in flow of heat. If it is desired to make the results precise, some method would be required to control the flow of heat between the source and sink, and to prevent loss of heat from the sides of the plates.

ABSTRACT.

If a sheet of tinned iron be heated locally by means of a Bunsen burner or blowpipe the tin is melted for a certain distance from the heated region. On allowing the sheet to cool the resolidified tin is separated from the unmelted tin by a very sharp line of demarcation. This line gives us the equi-temperature curve corresponding to the melting-point of tin. By pushing the heating to a greater or less extent a series of such equi-temperature curves can be obtained for a sheet of any particular shape heated at any given point. The cases shown illustrated the flow of heat into a rectangular plate from a heated tongue ; into a circular disc from a heated tongue ; round the corner of an L-shaped strip and into the vanes of an air-cooled cylinder. The results were shown to be closely analogous to the flow of electricity in similarly shaped conductors.

DISCUSSION.

Dr. R. S. **Willows** said a similar method had already been used by Voigt and his students to compare the thermal conductivities of different metals. They employed an organic substance which melted about 41°C. and gave a very sharp line on resolidification. Their method of heating was to place the metal strip on a red-hot copper block.

The **President** asked if the change of colour of mercuric iodide could not be used for this purpose.

Mr. **Ezer Griffiths** mentioned that if a sheet of steel be heated at the centre by means of a blow-pipe, then, on cooling, a bright circular wave may be seen travelling towards the centre due to recalescence. The converse effect was said to be observed during heating. The heat-indicating paints were the double iodides of copper-mercury (scarlet) and silver-mercury (yellow). Both darkened on heating, the former at 87°C. and the latter at 45°C., the change being reversible. They could be prepared by adding a solution of $CuSO_4$ or $AgNO_3$ to a solution of KI, redissolving the precipitate and adding a solution of $HgCl_2$. Experiments involving the use of these paints are described in "Light, Visible and Invisible," by Prof. S. P. Thompson.

The AUTHOR said he was glad to hear about Voigt's experiments. He had seen the recalescence experiment mentioned by Mr. Griffiths. One trouble with paints used as heat indicators was that there was usually a considerable lag between the temperatures at which the change took place on heating and on cooling. Moreover, the line of demarcation was not very sharp.

XIII. *The Absorption of Gas by Quartz Vacuum Tubes.* By R. S. WILLOWS, *M.A., D.Sc., and* H. TREVELYAN GEORGE, *M.A.*

RECEIVED MARCH 14, 1916.

IT is a common experience to those who work with vacuum tubes that, once the electrodes are freed from gas, the continued passage of a discharge lowers the pressure, and the tube eventually evacuates itself to such an extent that further discharge becomes impossible. This gives rise to much trouble in X-ray technique and, as gas-pressure regulators have to be added, complicates the construction of the tubes. These disadvantages have only recently been surmounted in the well known, but costly, Coolidge tube. It is, therefore, a matter of great practical importance to gain some knowledge of this process of self-evacuation.

The first systematic investigation appears to be that of Willows,* who came to the conclusion that the absorption was the result of chemical actions between the gas and the walls of the tube. The fact that nitrogen was absorbed as well as other gases was at that time a theoretical difficulty, which the subsequent researches of Prof. Strutt on active nitrogen have finally removed. Vegard† has drawn from Willows' results the conclusion that the gas is driven into the cathode ; but he apparently failed to note that absorption is also produced by the *electrodeless* ring discharge. Campbell Swinton‡ thinks that the occlusion is entirely a mechanical effect, the gas being fired into the glass, like a bullet into a target, and retained there. He supports his theory by some striking and beautiful experiments. S. E. Hill§, at Willows' suggestion, used the electrodeless discharge in a number of bulbs made of different kinds of glass, and comes to the conclusion that chemical effects are capable of explaining the results.

One feature of Hill's experiments, which has a bearing on the observations which follow, is the fact that a bulb can be fed with a gas, *e.g.*, hydrogen, until its appetite is very greatly diminished, but can be restored to its original activity by allowing it to absorb another gas, *e.g.*, air. This, together with the fact that different glasses absorb in very different degrees, in our opinion points clearly to chemical action as, at least, one of the main causes of the absorption.

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* "Phil. Mag.," April, 1901.

† "Phil. Mag.," 18, 477, 1909.

‡ "Proc." Roy. Soc., 81, 453, 1908. Other references to Mr. Swinton's work will be found here.

§ "Proc.," Phys. Soc., Dec., 1912.

The present communication is a continuation of Hill's work. Owing to the chemical inertia of quartz it was considered that experiments on a tube of this material would be of interest. A spherical bulb 7-8 cm. in diameter was used; it was connected through a mercury seal to a pump and a McLeod gauge reading to 1/500 mm. An electrodeless discharge was produced in the usual manner by means of a 6 in. coil. The zinc discharge knobs were carefully polished at frequent intervals in order to keep the current through the gas as steady as possible; with the same object the coil was driven by a mercury-jet interrupter and the spark was blown out by an air blast.

The method of making observations was as follows: After proper preparation the tube was mounted on the apparatus, washed out several times with the gas to be used, and pumped down to a pressure at which the discharge would pass. For air this was about $\frac{1}{3}$ mm., but for hydrogen about 1 mm. The coil was run for a certain interval and the change in pressure that the discharge had produced was noted on the gauge; if necessary the pressure was then slightly reduced before further observations were made. In this way the whole range of pressure was covered in which an electrodeless discharge was possible. In the tables below the pressures are given in gauge readings. Initially the first bulb was cleaned out with chromic acid and distilled water before it was used. In the early experiments, in which air was used, it was thought that the problem of stopping the absorption was finally solved; for a discharge was passed under various pressures for a total period of several hours without causing the slightest absorption; there was, if any change at all, a very slight increase in the pressure. When, however, the bulb was washed out with hydrogen the discharge immediately caused an absorption of gas, as is seen from the Table below.

TABLE I.—*Showing the First Absorption of Hydrogen.*

Period of discharge in mins.	Mean pressure.	Decrease in pressure.
10	163	4
20	122	2
15	94	nil

A fresh charge of hydrogen was allowed to stand in the apparatus for a few hours and further observations were made. This was repeated with fresh supplies of gas in succeeding days, during which it was noticed that the activity of the quartz was gradually increasing, until it finally reached a maximum and then gradually decreased. This is shown in Table II.

TABLE II.—*Showing the Absorption of Hydrogen a few days later than in Table I.*

Period of discharge.	Mean pressure.	Decrease of pressure.
10	242	5
10	182	5
10	136	5
5	100	12
10	70	42
10	32	25
4*	14	3
* The discharge failed to pass after this interval.		
A few days later.		
10	107	2
10	72	9
10	49	6
10	31	4

During the last set of readings it was noted that the discharge was exceptionally good ; the failure to absorb so readily as before cannot, therefore, be ascribed to faulty conditions of the experiment.

These Tables agree with Hill's experiments in showing that the appetite of a tube for hydrogen can be greatly diminished after a certain stage. This agreement extends still further, for the bulb was now filled with air and a discharge passed, when it was found that if the pressure was less than 90 the absorption was as large as, and sometimes larger than, with hydrogen. At pressures greater than 90 the current usually caused a very slight evolution of gas. Although the experiments were run for several days very little fatigue effect was noticed with air. Further fillings with hydrogen showed that this gas was now very actively absorbed.

A review of all the experiments shows that, no matter what the treatment to which the bulb has been subjected, the discharge never causes the pressure to rise when hydrogen is used, except for a few doubtful increases which occur when the gas has been standing at a considerable pressure in the bulb for some time. These exceptions may easily be due to gas condensed on the walls. With air slight evolutions nearly invariably take place at pressures greater than 100, while at lower pressures gas is gradually absorbed.

It will be seen from this description that our results with quartz are very similar to those of Hill with glass. The chief difference is that, in our experiments, a bulb has become actively absorbent for air although it was altogether inactive initially.

A possible explanation of this last result might be the presence of a layer of hydrogen condensed, or more properly speaking, adsorbed on the walls of the bulb, either on account of electrical attractions or from some other cause. It is well known that such layers of gas do exist when a bulb is first exhausted. The air might then combine with this and so apparently be absorbed, as any water vapour would be taken up in the drying bulbs. Such a layer of air or hydrogen might also account for the evolution at the higher pressures, for the heat of the discharge may possibly drive off gas to such an extent as to mask the absorption.

The following experiment shows that this is not the correct explanation of the absorption of air. The quartz bulb was made red hot and the evolved gas was pumped off until further heating caused no change in the pressure. On admitting a small quantity of air and discharging the coil the absorption was found to be larger than ever. It may also be mentioned that similar heat treatment was applied to the bulb when it was first received, without, as has been shown, causing the slightest adsorption of air. The hydrogen, if present, must therefore be in the combined condition; and further, when the bulb was blown the treatment was such as to leave it free from combined hydrogen. It must also be remembered that, according to Freundlich*, both oxygen and nitrogen are much more strongly adsorbed than hydrogen. Table III. shows the absorption of air after the bulb had been strongly heated, pumped out, and a small quantity of air re-admitted.

TABLE III.

Period of discharge in mins.	Mean pressure.	Decrease in pressure.
4½	43	51
4½	38	41
1¼	38	20

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* "Kapillarchemie," p. 96, *et seq.*

When the bulb had been treated in this manner it was found that further heating caused an evolution ; but a similar effect was found even without the discharge, and is no doubt due to gas adsorbed on the walls. It is uncertain whether all the absorbed gas can be recovered by heating ; this, together with further details, we hope to investigate later.

Our experiments with this bulb remind us strongly of the formation of the active plates in a Planté accumulator, if the absorption of air be taken to correspond to the discharge of the cell and that of hydrogen to the charging. Just as, initially, the cell must be charged before it can supply a current, so must hydrogen be absorbed before an absorption of air takes place ; and as these processes are alternated the surfaces of both cell and bulb become more active.

A second bulb was now tried, hydrogen being the first gas used. Observations were made from pressures of 200 downwards, but to save space only a few of these are given in Table IV.

TABLE IV.

Period of discharge in mins.	Mean pressure.	Decrease in pressure.
5	117	7
5	110	3
5	80	1
5	61	1
5	48	0
5	36	0
5	21	0

The Table shows that the absorption was small and had a definite limit but, as before, it gradually increased with successive doses of hydrogen. When a few charges had been absorbed air was admitted and was found to disappear from the first. The second bulb, in fact, behaved exactly like the first did after hydrogen had been absorbed.

In spite of the chemical inertness of quartz we regarded chemical actions between the gases of the discharge and the bulb as, at least, a possibility. If they involved the quartz directly our experiments might be explained as follows: Initially the walls consist of SiO_2, and if this cannot be further oxidised no air absorption should occur. This is what takes place. When hydrogen is admitted and the discharge is passed it may first reduce some of the silica and may then form silicon hydride. If the hydrogen is now replaced by air both oxygen and nitrogen are absorbed ; hence we must suppose that not only is the oxide reformed, but compounds containing nitrogen (nitrides ?) also appear. We tried to bring about similar effects by chemical treatment. The bulb was washed out with stannous chloride with the idea of reducing any oxidation product that had been formed, and thereby diminishing the absorption of hydrogen. Tests showed that this did not produce any clearly marked effects at first, but as they progressed it appeared that the appetite of the tube for hydrogen was now more easily satisfied.

A similar, but more marked effect, was found if the stannous chloride was replaced by SO_2 solution ; after three charges the bulb refused to absorb hydrogen from a pressure of 100 downwards—the region where previously the absorption was most strongly marked.

Hot aqua-regia was also used with the idea of reducing the absorption of air, but we did not succeed in doing this. The aqua-regia brought about more quickly the state in which hydrogen is not absorbed. It is, therefore, doubtful whether these effects are genuine chemical effects ; they may rather have produced adsorbed layers of gas on the bulb, whose gradual release masks the absorption. This point and others connected with adsorbed gas were under consideration when the work had to be suspended, but we hope to return to them later. The matter should prove easy to settle in the case of a substance which can be so strongly heated as quartz.

With regard to the relation of our experiments to those of Mr. Swinton we propose to say very little. Even when the electrodes in his experiments are outside the tube there is considerable bombardment of the glass and intense local heating, and it is doubtful whether we are testing the same effects as he does.

It was thought at one time that there were visible chemical changes on the surface of the bulb, as sometimes there appeared a black deposit at the neck of the bulb and, less frequently, in the plane of the discharge. This has also been noticed by Hill. It was found to be readily soluble in cold aqua-regia and was volatilised below a dull red heat ; most probably it is some compound of mercury. It is unlikely to be silicon as the melting point of this element is 1,400°C. We tried to keep mercury vapour out of the bulb by packing the leading tube with gold leaf, but this did not prove a satisfactory filter, as examination with a Hilger wave-length spectroscope readily showed. We understand that the absorptive power of the leaf depends on its physical condition; only annealed leaf is a satisfactory absorbent. Various annealings, however, still left us unsuccessful.

While examining the spectrum we were interested to note the way in which the hydrogen spectra varied in intensity. At about 1 mm. pressure the primary spectrum of hydrogen was all that could be seen; this at first increased in intensity as the pressure was lowered, then gradually disappeared. At the same time the mercury spectrum became more prominent and also a very fine secondary spectrum of hydrogen appeared. This could only be seen at a distance of a few millimetres from the walls, *i.e.*, in the strongest part of the ring discharge.

ABSTRACT.

The experiments are a continuation of those of Willows ("Phil. Mag." April, 1901) and Hill ("Phys. Soc.," December, 1912) on the absorption of gas which is brought about by electrical discharges. A new quartz bulb does not absorb air, but if it be fed with repeated doses of hydrogen—which are absorbed when an electrodeless discharge is passed—it then becomes very active. If discharges in hydrogen are alternated with those in air the bulb can be made to absorb large quantities of either gas, and the activity with each gradually increases. The authors reject the theory of surface absorption and, in their own experiments at least, also Swinton's theory that the gas is shot into the walls and held there. It is supposed that chemical actions occur with air, and oxidation products are formed; these are reduced by hydrogen. The process is compared with the formation of the plates in a Planté cell; the absorption of hydrogen corresponding to the charging, and that of air to the discharging of the cell. Attempts to produce the same effects by chemical treatment are partially successful, particularly in fatiguing the bulb so that no further absorption takes place. The conditions under which the primary and secondary hydrogen spectra appear are also described.

DISCUSSION.

Mr. A. Campbell Swinton said he was very much interested in the subject. It was true that most of his experiments were done with tubes having electrodes and there was very considerable heating. Under the bombardment of the cathode particles the inner surface of the glass may attain a very high temperature for a very short space of time. Sir J. J. Thomson had thought that it might almost become fluid and absorb the gas by ordinary diffusion. Sir J. Larmor, on the other hand, had conceived the molecules of gas to be hammered into the glass like tin tacks by the cathode particles. Some of his experiments had been done with external electrodes of tinfoil tied round the outside of the tube. He had also obtained absorption of helium which was not known to combine chemically with anything.

Dr. Bryan described some experiments he had been making with a vacuum valve at pressures less than 1/1000th mm. Normally the electrodeless discharge will not work at this pressure, but it does so when a current is passed through the glower (tungsten filament). Under these circumstances the pressure rises, although, after the valve has been running for some time, the current in the filament when running by itself produces a decrease in pressure.

Dr. Eccles, referring to the failure of gold leaf in certain circumstances to absorb mercury vapour, said that some workers were using silver for this purpose. It seems to have been used successfully for reducing mercury vapour pressure down to, but not beyond, a certain limiting vapour pressure.

Dr. H. S. Allen said that if a tube were coated with silver by spluttering from silver electrodes, the layer so obtained was said to absorb mercury vapour very readily.

Dr. Willows, in reply, said that Mr. Campbell Swinton's results with helium were not conclusive, as it was not certain that they were dealing with the same phenomenon. The discharge in a tube with external electrodes was not an electrodeless discharge at all. There was still cathode ray bombardment and strong local heating. It would be interesting to see if the experiments with helium could be repeated with a true electrodeless discharge free from any electrostatic effects. He thought Dr. Bryan's results could all be accounted for by gas coming out of the metal itself. He had not used silver to absorb mercury vapour because of the difficulty of getting it free from air. Mr. Harlow about two years since showed the Society an experiment similar to the one described by Dr. Bryan.

XIV. *A New Method of Determining Ionic Velocities.* By

CONSTANCE HARRISON GRIFFITHS, *B.Sc., Research Student, Birkbeck College.*

RECEIVED FEBRUARY 25, 1916.

INTRODUCTION.

THE object of the research was to test the practicability of a method of determining ionic velocities, which can be carried out with the resources of an ordinary physics department and which requires little or no skill in chemical manipulations.

The electrolyte chosen for the tests was an aqueous solution of copper sulphate.

In the Hittorf and kindred methods the changes in the electrolyte produced by the passage of the current are determined by chemical analysis; in the method to be described the total change in weight of the cathode and the electrolyte in its neighbourhood is obtained by direct weighing, and allowances are made for the change in volume of the cathode and for the changes in volume of the liquid surrounding the cathode, as it changes in density. The cathode was situated in a cylindrical vessel closed at the upper end and open at the lower end.

The cathode and the containing vessel were suspended from the arm of a balance and hung in a tank containing an aqueous solution of copper sulphate.

THEORY OF THE METHOD.

Let the diagram represent the cathode and the containing vessel.

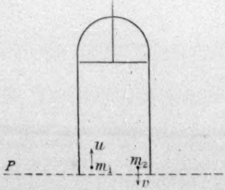


FIG. 1.

Let m_1 be the mass of the cations per cubic centimetre.
,, u cms./sec. be the component of their velocity upwards relatively to the liquid.

Let m_2 be the mass of the anions per cubic centimetre.

" v cms./sec. be the component of their velocity downwards relatively to the liquid.

" c=the current in amperes.

" A=area of cross-section of the lower end of the electrode vessel in square centimetres.

Consider passage of ions across the section P.

Then *loss of weight* in electrode vessel per second would equal

$$(m_2v-m_1u)A \text{ grammes}$$

if the liquid were at rest. Allowance must be made for the movement of the liquid.

Let q=the quantity in coulombs of electricity required to deposit 1 gramme of cations; then mass of deposit per second $=c/q$ grammes.

If the density of the deposit is d, *increase of volume of electrode* per second$=c/qd$ cubic centimetre.

Total mass of salt in cathode vessel diminishes at the rate of $(m_1+m_2)Av$ gms./sec., since m_2Av grammes of anion leave the vessel per second, and there are always equal numbers of $+^{ve}$ and $-^{ve}$ ions in the liquid in the cathode vessel. When a salt is dissolved in water there is in general an *increase in volume.*

Let δ=the increase in volume produced by dissolving 1 gramme of salt.

Then decrease in volume of solution in vessel$=(m_1+m_2)Av\delta$ cubic centimetres.

$\therefore$ Total decrease in volume in vessel$=(m_1+m_2)Av\delta-c/qd$ cubic centimetres.

Unchanged liquid to this amount will, therefore, enter the vessel, and if its density is ρ the gain in weight will be

$$\left\{(m_1+m_2)Av\delta-\frac{c}{qd}\right\}\rho \text{ grammes.}$$

$\therefore$ Total loss in weight of the suspended system

$$=(m_2v-m_1u)A-\left\{(m_1+m_2)Av\delta-\frac{c}{qd}\right\}\rho \text{ grammes} \quad . \quad (1)$$

This is one relation. Now there is a second relation.

Let N=number of gramme equivalents of copper per cubic centimetre and e=quantity of electricity associated with 1 gramme equivalent; then

$$Ne(u+v)A=\text{total current in amperes.} \quad . \quad . \quad (2)$$

Summary.—Therefore we have the two equations

1. $(m_2v-m_1u)A-\left\{(m_1+m_2)Av\delta-\frac{c}{qd}\right\}\rho$

=total loss of weight of suspended system per second.

2. $$Ne(u+v)A=c.$$

SECOND METHOD OF CONSIDERING THEORY.

Let a=absolute velocity of cations upwards.
b=absolute velocity of anions downwards.
x=velocity of liquid upwards across the lower end of the cathode vessel.
n=concentration in gms./cc. of solution.

And let the remaining symbols have the same meaning as before Then, clearly,

$$a=u+x$$
$$b=v-x.$$

Consider the passage of ions across the section P, *i.e.*, across the lower end of the tube.

The total mass of anions crossing the section downwards equals m_2bA per second, and the total mass of cations crossing the section upwards equals m_1aA per second.

Thus the loss in mass per second of the cathode vessel due to the movement of the ions equals $(m_2b-m_1a)A$.

Since m_2b of anions leave the cathode vessel, and since there must be a corresponding loss of the cations in solution in the cathode vessel, it follows that $(m_1+m_2)bA$ equals the diminution in the quantity of salt in solution in the cathode vessel. There is a gain in the quantity of water in the cathode vessel owing to the velocity x of the liquid upwards.

This gain per second=$xA(\rho-n)$; since $(\rho-n)$ is the mass of water per cubic centimetre of solution.

Thus total loss of weight of cathode vessel per second equals

$$(m_2b-m_1a)A-xA(\rho-n).$$

When a salt is added to a solution there is in general an increase in volume of the solution.

Let δ=the increase in volume produced by dissolving 1 gramme of salt. As is shown above, $(m_1+m_2)bA$ equals the mass of salt extracted per second, as the result of the electrolytic operations, from the cathode vessel.

But the liquid moves upwards x centimetres per second, and introduces $x(m_1+m_2)A$ grammes of salt into the cathode vessel.

Thus, the salt lost by the solution originally in the cathode vessel equals $(m_1+m_2)bA+x(m_1+m_2)A$;

$$i.e., \quad =(m_1+m_2)(b+x)A, \quad \text{or } (m_1+m_2)vA.$$

It is clear that the diminution in volume due to the diminution in the salt in the cathode vessel equals $(m_1+m_2)vA\delta$. Account must now be taken of the change in volume of the cathode. Then, as before, the increase in the volume of the cathode per second equals c/qd.

Thus
$$xA=(m_1+m_2)vA\delta-\frac{c}{qd}.$$

Substituting this value of xA in the expression for the rate of loss of total weight of the cathode and cathode vessel we obtain

$$(m_2b-m_1a)A-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n).$$

Substituting $a=u+x$ and $b=v-x$ we obtain

$$(m_2v-m_1u)A-(m_1+m_2)xA-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n),$$

$$i.e., \quad (m_2v-m_1u)A-(m_1+m_2)\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}$$
$$-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n),$$

$$i.e., \quad (m_2v-m_1u)A-n\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}$$
$$-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho-n),$$

$$i.e., \quad (m_2v-m_1u)A-\left\{(m_1+m_2)vA\delta-\frac{c}{qd}\right\}(\rho), \quad . \quad . \quad (1)$$

which is the same equation as was obtained by the other method of considering the theory.

By reasoning exactly similar to that used in the first method we obtain

$$Ne(a+b)A=c;$$
whence
$$Ne(u+x+v-x)A=c,$$
and
$$Ne(u+v)A=c \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is exactly the same as the second equation previously obtained.

APPARATUS.

In the diagram B is the plan of a balance from which hangs the cathode K and the cathode vessel C.

A is the anode and anode vessel, and T the tank which contains the solution used for the experiment.

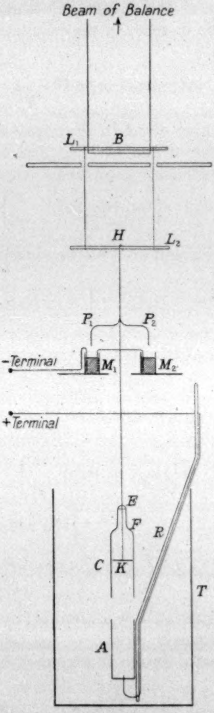

Beam of Balance
L₁
B
H
L₂
P₁
P₂
-Terminal
M₁
M₂
+Terminal
E
F
R
C
K
T
A

FIG. 2.

DETAILS OF APPARATUS.

Cathode.—The cathode consists of a disc of copper 2·7 cm. diameter, perforated by two holes. It fits loosely into the cathode vessel C. The *cathode vessel* consists of a glass tube 8·9 cm. long and 2·7 cm. diameter, open at the lower end. At the upper end the cathode vessel is narrowed and terminates in a piece of 2 mm. bore tubing about 3 cm. long. The cathode is situated about halfway up the cathode vessel, so that the weaker solution produced by the passage of the current may pass through the holes in the cathode and to the top of the cathode vessel.

Suspension of Cathode.—The cathode vessel and the cathode are suspended by means of gutta-percha-coated copper wire. This wire is attached to the cathode at its lower end by being scraped clear of insulation at that point and threaded backwards and forwards through four holes bored near the centre of the cathode.

The insulated wire passes vertically up from the cathode and through the 2 mm. bore tubing EF, into which it fits somewhat tightly, and into which it is sealed at the top with a small quantity of Chatterton cement.

Thus the cathode vessel is completely closed at the top. About 34 cm. above the cathode vessel the suspension wire terminates in a hook which passes over a glass rod suspended from a balance pan.

Electrical connection with the cathode is effected by means of two plantinum points attached to the suspension wire near the top.

Anode.—The anode consists of a spiral of thick copper wire with a lacing of thin wire across two diameters to hold the turns of the spiral in place.

From the centre of the spiral and continuous with it, being part of the same wire from which the spiral was made, a wire passes down vertically till clear of the anode vessel, then bends round and passes up through the liquid and out at the top of the tank.

All this wire, after it leaves the anode spiral, is coated with gutta-percha insulation.

The *anode vessel* consists of a piece of glass tubing 8 cm. long and 2·7 cm. diameter. The anode just fits inside it at the lower end.

Support Rod.—The wire to the anode vessel and the anode vessel itself are bound tightly to a bent glass rod, R, which supports them and holds them in the required position. This rod is clamped above the level of the top of the tank by two firm clips which are carried by a vertical bar fixed in a strong stand.

The anode vessel is set vertically under the cathode vessel so that the distance apart of the two vessels is about 3 cm. This is done before the tank is placed in position.

Current Leads to Cathode.—The suspension wire of the cathode is cleared of insulation at a point near the top, and round it at this point are tightly wrapped two pieces of copper wire. These are bent as in the diagram and terminate in two platinum points. These platinum points dip into two cups of mercury connected together by a thick copper wire. Into one of these cups dips a wire connected to the negative terminal of the cell.

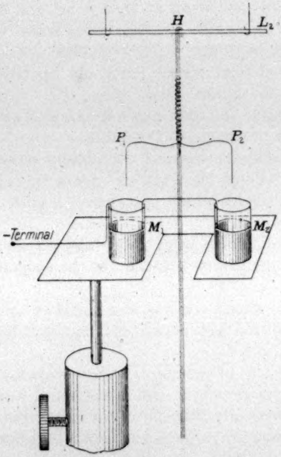


Fig. 3.

The mercury cups are supported by a shelf of wood fixed to a stand of adjustable height. By raising the stand till the platinum points are immersed in the cups the current is allowed to pass. On lowering the stand the points hang free in air, and weighings can be made by means of the balance.

Balance.—The balance used was a Sartorius, and would weigh with accuracy to 0·0001 grammes. It is enclosed in a case in the floor of which two holes were bored beneath and slightly to each side of the left-hand pan. Across the left-hand pan is placed a glass rod painted with shellac. Over this are hooked two short wires of copper, one at each end. These wires pass vertically down, one through each of the two holes in the floor of the case. At the lower end of each is a hook, and these hooks support another glass rod similar to the first. From the centre of this second rod hangs the cathode and cathode vessel by means of the hook at the top of the suspension wire.

Tank.—The tank is a large cylindrical glass jar 29 cm. high, 19 cm. diameter, having a capacity of 8 litres approximately. This tank contains the solution of copper sulphate used for the experiment.

Over the surface of the solution is placed a layer of castor oil (about 100 cubic cm.), for it was found that the weighings taken by means of the balance were very inaccurate when the suspension wire passed straight into the copper sulphate solution from the air, but that when the layer of castor oil was placed over the surface the weighings were very consistent.

The temperature of the solution in the tank is taken by means of a thermometer suspended in the solution, so that its bulb is close to the cathode vessel.

General Arrangement of Apparatus.—The foregoing apparatus—tank, balance, cathode, anode, &c.—are arranged in a thermostat room kept at a constant temperature by means of a thermostat-regulated gas stove.

The wires from the cathode and anode are connected to two terminals, and from these wires proceed to a table outside the thermostat room.

On this table is arranged the rest of the circuit, consisting of a 4-volt secondary cell, a key, an adjustable resistance and a Paul millivoltmeter in parallel with 1 ohm.

Method of Procedure.—The copper sulphate solution was prepared, placed in an aspirator and the air exhausted from it by connecting the top of the aspirator to an exhausting pump for one hour. This was done to prevent any formation of bubbles in the tank. The solution was then kept under a vacuum until it was placed in the tank.

The tank was placed in position under the balance, the cathode being already suspended in position. The anode was moved from its position under the cathode by rotating the vertical bar to which the support rod was attached.

A bent capillary glass tube was now fixed so as to project through a hole in the cathode and to reach to the top of the cathode vessel on the inside. The other end of this tube reached above the level of the top of the tank, and was attached to a rubber tube. Through this capillary tube the air in the cathode vessel was withdrawn.

The solution was then run slowly into the tank through a glass tube reaching to the bottom of the tank. When the surface of the liquid reached the cathode vessel air was withdrawn through the capillary tube, so as to keep the levels of the solution inside and outside the cathode vessel approximately the same.

When the tank was full to within 2 cm. of the top, and all the air withdrawn from the cathode vessel, the capillary tube was removed. The anode was brought back to its correct position and the castor oil was poured on the surface of the liquid.

A thermometer was suspened in the solution and the apparatus was usually left till the next day. On the next day a *weighing of the suspended cathode vessel and cathode* was made and the time noted.

After an interval of about one hour *another weighing was taken* at a noted time. The temperature was also read. The *mercury cups* were then raised so as to make contact with the platinum points, and the current was put on at a definite time and rapidly adjusted to the desired value.

Readings of the current and the time were then taken at intervals. The temperature was also read at intervals.

After a time, which varied from about two hours in the case of the more concentrated solutions to four hours in the case of the less concentrated solutions, the current was stopped at a certain definite time. The mercury cups were lowered and the weight was rapidly taken. After about one hour another weighing was taken to get the rate of change of the weight after the experiment.

The mean of this rate of change and the rate of change before the experiment was taken to be the average rate of change of weight during the course of the experiment, and was applied as a correction to the observed change of weight.

The average current during the time of the experiment was found by taking the average current over the intervals between each two consecutive readings, multiplying each of these averages by the number of minutes in that interval, and finally obtaining the average current per minute from all the results so obtained.

To the results so obtained a correction was made for the zero of the ammeter.

Weighing of the undisturbed cathode vessel and contents made the day after an experiment showed that the change of weight due to diffusion into the cathode vessel might safely be neglected, and proved also that there was no appreciable change in the concentration of the solution towards the lower end of the cathode vessel in the course of an experiment.

SPECIMEN EXPERIMENT.

Experiment No. 12.—

Density of solution (found by means of a specific gravity bottle)=1·0273.

Time.	Weight.	Current reading in milliamperes.	Temp.
2–5	33·4360	......	20·00
2–48	33·4360	......	20·00
	Mercury cups raised.		...
2–52	...	Current started.	...
2–52–10	...	30·1	...
2–53	...	30·2	...
2–55	...	30·4	...
2–56	...	30·5	...
2–58	...	30·6	...
3– 0	...	30·6	...
3–10	...	30·7	...
3–20	...	30·8	...
3–35	...	30·8	...
3–40	...	30·8	...
4– 0	...	30·8	...
4– 6	...	30·8	...
5– 0	...	30·8	...
5–11	...	30·8	...
5–37	...	30·8	...
5–44	...	30·8	...
5–45	...	Current stopped.	...
	Mercury cups lowered.		...
5–49	33·3499	......	19·95
7–33	33·3504	......	19·90

Time of passage of current=173 minutes.

Average value of current (corrected for zero of ammeter) =0·03285 amperes.

Change of weight—

Rate of change of weight before experiment=zero

" " " after " $= \frac{0{\cdot}0005}{104}$ gm./mt. increase.

$$\therefore \text{ Corrections} = -\frac{0{\cdot}0005}{104\times 2}\times 181 \text{ grammes.}$$

∴ Corrected change of weight during experiment
$=33{\cdot}4360-33{\cdot}3499+0{\cdot}000435=0{\cdot}0865$ grammes.

$\rho=1{\cdot}0273$. ∴ $n=0{\cdot}028205$ (by interpolation from tables in Landolt and Börnstein).

$$\therefore \quad m_1=\frac{0{\cdot}028205\times 63{\cdot}6}{159{\cdot}66}=0{\cdot}01124 \text{ gm./cc.}$$

and $m_2=0{\cdot}01697$ gms./cc.

To find δ—

$$\delta=\frac{\text{increment in volume}}{\text{increment in salt}}.$$

If ρ=density and n concentration per cubic centimetre in grammes, let

Mass of water=1 gramme.

Then Mass of salt$=\frac{n}{\rho-n}$grammes.

Total mass $=1+\frac{n}{\rho-n}=\frac{\rho}{\rho-n}$;

Total volume $=\text{mass}\times\frac{1}{\rho}=\frac{1}{\rho-n}$;

$$\therefore \quad \delta=\frac{\frac{1}{\rho_2-n_2}-\frac{1}{\rho_1-n_1}}{\frac{n_2}{\rho_2-n_2}-\frac{n_1}{\rho_1-n_1}}=\frac{(\rho_1-n_1)-(\rho_2-n_2)}{n_2(\rho_1-n_1)-n_1(\rho_2-n_2)}.$$

In this case (from tables), when

$\rho_1=1{\cdot}0254$, $n_1=0{\cdot}026209$,
$\rho_2=1{\cdot}0384$, $n_2=0{\cdot}039812$,

substitute these values in above formula; then

$$\delta=0{\cdot}04431.$$

Collecting data:

$m_1=0{\cdot}01124$ gm./cc. $m_2=0{\cdot}01697$ gm./cc.
$\delta=0{\cdot}04431$ $\rho=1{\cdot}0273$
$q=3045$ $d=8{\cdot}952$
$c=0{\cdot}03285$ ampere.

$$\text{Loss of wt./sec.}=\frac{0{\cdot}0865}{173\times 60}=8{\cdot}333\times 10^{-6}$$

$$N=\frac{0{\cdot}028205}{79{\cdot}83}$$

$$e=96{,}550.$$

$\therefore$ in equation (1), $m_2V-m_1U-n\delta\rho V+\frac{c\rho}{qd}=$loss of weight/sec. (where $V=vA$ and $U=uA$).

1st term $\quad m_2V=0{\cdot}01697V$
2nd ,, $\quad m_1U=-0{\cdot}01124U$
3rd ,, $\quad -n\delta\rho V=-0{\cdot}001283V$
4th ,, $\quad \frac{c\rho}{qd}=1{\cdot}238\times 10^{-6}.$
5th ,, $\quad$ Loss wt./sec. $=8{\cdot}333\times 10^{-6}$

$$\therefore \qquad 0{\cdot}01568V-0{\cdot}01124U=7{\cdot}095\times 10^{-6} \quad . \quad . \quad (\text{A})$$

and in equation (2) $Ne(V+U)=c$.

$$U+V=\frac{c}{Ne}=9{\cdot}632\times 10^{-4}.$$

$$\therefore \qquad V=9{\cdot}632\times 10^{-4}-U \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{B})$$

Substitute in equation (A) for V.

$$\therefore\ 0{\cdot}01568\times 9{\cdot}632\times 10^{-4}-0{\cdot}01568U-0{\cdot}01124U=7{\cdot}095\times 10^{-6}.$$

$$\therefore \qquad 0{\cdot}02692U=0{\cdot}8005\times 10^{-5}.$$

$$\therefore \qquad U=2{\cdot}974\ \times 10^{-4}$$
$$V=6{\cdot}658\ \times 10^{-4}.$$

A, the area of the end of the cathode vessel$=5{\cdot}9768$ sq. cm.;

$$\therefore \qquad u=4{\cdot}975\ \times 10^{-5}$$
$$v=1{\cdot}114\ \times 10^{-4}$$

and $\qquad \frac{v}{u+v}=0{\cdot}6910. \qquad$ Temperature$=19{\cdot}90$°C.

The value of q, the quantity of electricity in coulombs required to deposit 1 gramme of cation, was found by means of a separate experiment, using the same apparatus and a similar cathode *not* enclosed by a cathode vessel; d was obtained from tables.

The area of the end of the cathode vessel A was found by placing a glass scale in millimetres across the end of the tube, so that the scale was in contact with the tube and reading the diameter of the tube by means of a microscope provided with a scale in the eye-piece. Eight readings were made along four diameters at intervals of 45 deg., and from these the value of *A* was calculated.

The zero of the ammeter was found by comparing the ammeter readings of a current with—

(*a*) An ordinary copper voltameter.

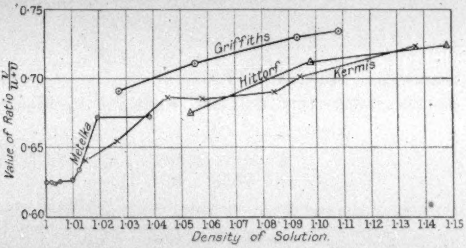
(*b*) A Cambridge thermo-electric potentiometer used across a standard ohm in the circuit and comparison being made against a standard Weston cell.

RESULTS.

A number of experiments were made with solutions of different concentrations, and the results are given in the table on p. 145.

CONCLUDING REMARKS.

It is extremely probable that the method can be employed in the case of other salts from which the metal can be electrolytically deposited on the cathode.



References to Tables of Results, from which curves have been drawn :—

Metelka—"Zeitschrift für Physikalische Chemie." Band XXXVII., 1901. Page 709. (Temp. 18°C – 19°C).

Kermis—"Annalen der Physik und Chemie." Band IV., 1878. Page 503 (Temp. 9°C – 24°C).

Hittorf—Landolt and Börnstein's tables. Edition III. (Temp. 6°C).

Griffiths—Average values deduced from table. (Temp. 19·6°C – 20·3°C).

FIG. 4.

In the case of a salt like potassium sulphate, for example, it is possible that the ionic mobilities could be determined by surrounding the copper anode of the cathode vessel with a solution of copper sulphate of somewhat smaller density than that of the solution of potassium sulphate, thus applying the

Table of Results.

Experiment.	Density	Concentration.	Current in amperes.	Time in seconds.	Change of weight in Gms./sec.	m_1	m_2	δ	u	v	$\frac{v}{u+v}$	Temp. Deg. C.
*1	1·0928	0·09827	0·08180	6,720	$2{\cdot}061 \times 10^{-5}$	0·03913	0·05914	0·08241	$3{\cdot}232 \times 10^{-5}$	$8{\cdot}285 \times 10^{-5}$	0·7190	20·10
*2	1·0928	0·09827	0·04094	7,200	$1{\cdot}097 \times 10^{-5}$	0·03913	0·05914	0·08241	$1{\cdot}497 \times 10^{-5}$	$4{\cdot}266 \times 10^{-5}$	0·7401	20·00
3	1·0928	0·09827	0·07198	9,052	$1{\cdot}867 \times 10^{-5}$	0·03913	0·05914	0·08241	$2{\cdot}751 \times 10^{-5}$	$7{\cdot}382 \times 10^{-5}$	0·7288	20·75
4	1·1083	0·11524	0·06387	8,340	$1{\cdot}673 \times 10^{-5}$	0·04587	0·06937	0·08241	$2{\cdot}054 \times 10^{-5}$	$5{\cdot}615 \times 10^{-5}$	0·7319	20·30
5	1·1083	0·11524	0·06691	8,640	$1{\cdot}772 \times 10^{-5}$	0·04587	0·06937	0·08241	$2{\cdot}120 \times 10^{-5}$	$5{\cdot}914 \times 10^{-5}$	0·7360	19·90
6	1·1083	0·11524	0·03280	15,600	$8{\cdot}553 \times 10^{-6}$	0·04587	0·06937	0·08241	$1{\cdot}074 \times 10^{-5}$	$2{\cdot}908 \times 10^{-5}$	0·7303	19·80
7	1·1083	0·11524	0·03229	13,500	$8{\cdot}583 \times 10^{-6}$	0·04587	0·06937	0·08241	$1{\cdot}017 \times 10^{-5}$	$2{\cdot}861 \times 10^{-5}$	0·7377	19·70
8	1·0554	0·05789	0·03357	13,200	$8{\cdot}484 \times 10^{-6}$	0·02305	0·03484	0·07092	$2{\cdot}322 \times 10^{-5}$	$5{\cdot}699 \times 10^{-5}$	0·7104	19·70
9	1·0554	0·05789	0·03349	15,000	$8{\cdot}4667 \times 10^{-6}$	0·02305	0·03484	0·07092	$2{\cdot}320 \times 10^{-5}$	$5{\cdot}683 \times 10^{-5}$	0·7114	19·80
10	1·0273	0·02821	0·03312	12,900	$8{\cdot}310 \times 10^{-6}$	0·01124	0·01697	0·04431	$4{\cdot}951 \times 10^{-5}$	$11{\cdot}26 \times 10^{-5}$	0·6942	19·30
11	1·0273	0·02821	0·03247	14,400	$8{\cdot}0972 \times 10^{-6}$	0·01124	0·01697	0·04431	$5{\cdot}000 \times 10^{-5}$	$10{\cdot}92 \times 10^{-5}$	0·6861	19·60
12	1·0273	0·02821	0·03285	10,380	$8{\cdot}333 \times 10^{-6}$	0·01124	0·01697	0·04431	$4{\cdot}975 \times 10^{-5}$	$11{\cdot}14 \times 10^{-5}$	0·6910	19·90

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* It may be noted that experiments (1) and (2) were of the nature of preliminary experiments, and that after experiment (3) a considerable number of improvements were made in details of the apparatus and in the method of conducting the experiments. These improvements were used in the subsequent experiments (4)–(12).

principle of the Daniell cell. There would be difficulties in determining δ, but the difficulties might not be insuperable.

Another method of determining the mobilities in the case of potassium sulphate would be to have a suspended anode vessel analogous in construction to the cathode vessel described in the Paper, and to have as an anode a metal which would go into solution when the current passes.

The results obtained by the author may be compared with those obtained by Hittorf, Metelka and Kermis by means of the curves drawn on the squared paper (diagram 4).

The comparison would appear to justify the method, but the divergence of the results obtained by previous workers would seem to show that if the progress of physics should demand an accurate knowledge of the values of migration constants very much more work will be required.

ABSTRACT.

In the experiments described the cathode, which consists of a horizontal copper disc perforated with two holes, is mounted in a cylindrical glass tube open at the lower end. The whole is suspended from the beam of a balance, and is immersed in a vessel of copper sulphate. The anode is a copper spiral fixed in the electrolyte some distance below the mouth of the cathode vessel. From the rate of change of weight of the suspended system during the passage of a current the ionic velocities can be determined.

DISCUSSION.

Mr. F. E. Smith admired the manner in which small difficulties had been overcome. Some years ago he had determined the electrochemical equivalent of silver with the anode suspended from the beam of a balance. If Mrs. Griffiths intended continuing these experiments, he would suggest the use of such salts as silver nitrate rather than copper sulphate.

Mr. J. H. Shaxby communicated the following remarks: It may be noted that the use of a relation, implicit in the reasoning but not actually employed, leads to a simple formula for calculating V without the necessity of separate determinations of m_1 and m_2. This saves a rather lengthy calculation, and incidentally avoids the necessity for relying on data in Landolt obtained by other workers. The relation is that the current $Ne(U+V)$ is also equal to $m_1q(U+V)$. (In fact, from the values given, $Ne=34{\cdot}36$ and $m_1q=34{\cdot}12$.) If, then, we substitute $\frac{c}{m_1q}-V$ for U in the equation

$$m_2V-m_1U-n\delta\rho V+\frac{c\rho}{qd}=W \text{ (loss in weight observed),}$$

we have
$$m_2V-m\left(\frac{c}{m_1q}-V\right)-n\delta\rho V+\frac{c\rho}{qd}=W,$$

or
$$V(m_1+m_2-n\delta\rho)=W+\frac{c}{q}-\frac{c\rho}{qd};$$

i.e.,
$$Vn(1-\delta\rho)=W+\frac{c}{q}\left(1-\frac{\rho}{d}\right).$$

The quantity δ is derived from the statement that "total mass of salt in cathode vessel diminishes at the rate of $(m_1+m_2)Av$ gms. /sec." Now this diminution is not by the elimination of salt *qua* salt, but in the form of already dissociated ions. The calculation of δ, from the variation of density of a solution with concentration, lumps together undissociated and dissociated salt. If we may suppose the ions to be of great density, the value of δ would be very small. If we neglect δ and re-calculate V, we find for experiments (12), (9), (3) and (6) respectively the values 6·339, 3·138, 4·011 and 1·561 ($\times 10^{-4}$), leading to the values for $\frac{v}{u+v}$ 0·6584, 0·6561, 0·6627 and 0·6634. For the lowest concentrations these agree with other workers' figures. Metelka's results for densities 1·019 and 1·038 suggest similarly constant values of $\frac{v}{u+v}$ for various concentrations, and are also in good agreement with Mrs. Griffiths' figures (as thus re-calculated).

Mrs. GRIFFITHS has communicated the following comments on Mr. Shaxby's remarks : The mathematics in the second and third paragraphs appears to be correct and is interesting, but the first paragraph would seem to be somewhat misleading in that the necessity is not avoided for relying on data (dealing with concentrations) obtained by other workers. Mr. Shaxby avoids the necessity by making an hypothesis in the last paragraph which is not justifiable, for when the current has ceased the value of δ cannot depend on the process whereby the salt has been eliminated. Even during the passage of the current the process can have only an inappreciable effect on the value of δ.

XV. *Note on an Explanation of the Migration of the Ions.* By

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Received February 21, 1916.

1. The object of this note is to attempt to remove an imperfection from a much-used graphical "explanation" of the phenomenon known as the migration of the ions.

The explanation in question proceeds briefly as follows: It is supposed that a solution of a salt MX is being electrolysed, that M is depositing upon the cathode C while X is similarly escaping from solution at the anode A, and it is desired to show that the rate of impoverishment of the solution round C is to that round A in the ratio $v : u$ of the ionic velocities of X and M. For this purpose a diagram of the following kind is drawn to represent (i.) the initial state of the electrolyte and (ii.) its state after a time t.

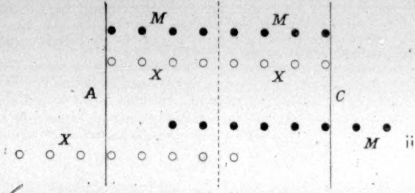

FIG. 1.

For purposes of illustration a simple ratio of u to v is chosen—*e.g.*, 2 : 3, as in the figure. It is now pointed out that the number of molecules to the left of the median line is fewer by two than the initial number, while the number to the right is fewer by three. Then it is said that it is seen in this way that three molecules are lost at the cathode, while two molecules are lost at the anode, and that, therefore, the cathode loss is to the anode loss as 3 : 2.

The same argument can be indicated more generally by a figure of the kind given below :—

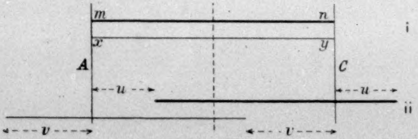

FIG. 2.

The initial string of positive ions is represented by the heavy line *mn*, and the corresponding string of anions by the lighter line *xy*. Taking u and v to be the respective velocities of the ions, the positions of the strings one second later will be as represented in the lower half of the figure, and, using the same argument as before, the decrease in the number of molecules to the left of the median line is to the decrease to the right in the ratio $u : v$.

2. The objection to this argument, however presented, is that, while it is made to give the correct result, it does not adequately represent what occurs. It ignores the cations left in solution near C and the anions left near A, and it is also silent concerning the inequality between the number of cations deposited upon C and of anions deposited upon A.* Further, even if we grant that the mechanism of electrolysis can be indicated in the simple way which the diagram suggests, molecules primarily concerned in the losses at the electrodes are omitted.

The truth of the matter is that no explanation of the relation between the electrode losses can be satisfactory if it does not emphasise the difference between the way in which the current is conveyed from one layer of the liquid to the next and that in which it is conveyed from the liquid to either electrode.

In the liquid the transference is partly by positive ions travelling in one direction, and partly by negative ions travelling in the opposite. At the electrodes, the transference is by ions of one kind only—by positive ions at the cathode and (in the simple case supposed) by negative ions at the anode.

In consequence of this, more cations are deposited at the cathode, and more anions at the anode, than those for which the ionic streams, due to the applied potential gradient, are responsible.

3. What happens may be represented symbolically in the following way :—

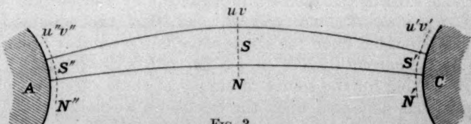

FIG. 3.

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* It is sometimes stated that the ions left unpartnered are supposed to be discharged and liberated.

In the figure let A and C represent sections of the electrodes, and let the curves extending between them represent the section of a tube bounded by current stream lines at any time t. Suppose for simplicity that the ions M and X are of equal valency and carry respectively the charges $\pm\varepsilon$. Let the potential gradient at any cross-section of the tube, of area S, be such that the ionic velocities are u and v respectively, and let N be the number of ions of each kind per unit volume near S. Let S', u', v', N' and S'', u'', v'', N'' be corresponding quantities for the sections S' and S'' in the immediate neighbourhoods of the electrodes.

Then the condition that there should be no accumulation of free electricity, in any element of volume of the tube, while the current flows, gives

$$SN(u+v)=S'N'(u'+v')=S''N''(u''+v''). \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The ratio of the ionic velocities is constant since these vary in the same way with the potential gradient.*

Hence, $\quad u/v=u'/v'=u''/v''$,

and, therefore, from (1)

$$SNu=S'N'u'=S''N''u'',$$

and $\quad SNv=S'N'v'=S''N''v''$.

The current across any section of the tube, at the time considered, is $SN(u+v)\varepsilon$ and the quantity of electricity conveyed through the solution, in the time dt, is $SN(u+v)\varepsilon dt$. During this time the number of cations deposited upon the cathode is, by Faraday's law, $SN(u+v)dt=S'N'(u'+v')dt$. Similarly, the number of anions deposited upon the anode is $SN(u+v)dt=S''N''(u''+v'')dt$. The number of cations brought by the current to the cathode in the same time is $S'N'u'dt$, and of anions to the anode $S''N''v''dt$.

Thus we see that the number of cations deposited upon the cathode exceeds the number brought up by the current by $S'N'(u'+v')dt-S'N'u'dt=SNvdt$, and that the number of anions deposited upon the anode exceeds the number brought up by the current by $S''N''(u''+v'')dt-S''N''v''dt=SNudt$.

In seeking for the source of supply of these excess cations and anions deposited upon the electrodes we notice that, in order to satisfy the equation (1), $S'N'v'dt=SNvdt$ anions must pass outwards through S′ and that $S''N''u''dt=SNudt$ cations must pass outwards through S''.

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* For the present purpose the fact that u/v may vary with N can be ignored.

Therefore, equation (1) will be satisfied if the following processes occur :—

During the deposition of $S'N'(u'+v')dt$ cations upon the cathode, $S'N'v'dt$ molecules dissociate (ionise) in the immediate neighbourhood of this electrode. The $S'N'v'dt$ cations of these molecules are deposited along with the $S'N'u'dt$ cations carried in by the cationic stream, while their $S'N'v'dt$ anions pass away from the electrode to maintain the anionic stream.

During the deposition, contemporaneous with that above, of $S''N''(u''+v'')dt$ anions upon the anode, $S''N''u''dt$ molecules dissociate in the solution in contact with this electrode and deposit their $S''N''u''dt$ anions along with the $S''N''v''dt$ anions carried to the anode in the anionic stream, while their $S''N''u''dt$ cations pass away from the electrode to maintain the cationic stream.

In this way during the passage of $SN(u+v)\varepsilon dt$ units of electricity through the solution, $SN(u+v)dt$ cations are deposited upon the cathode, and $SN(u+v)dt$ anions are deposited at the anode. The cathode space loses $SNvdt$ molecules, and the anode space loses $SNudt$.

Hence, we see at once that the ratio of the cathode loss to the anode loss, in any given element of time, is $v : u$, and we see also at once where the "lost" molecules have gone.

4. If it be urged, against the generality of this view of what occurs, that the requisite numbers of molecules may not always be present near the electrodes, or may not always ionise spontaneously to the required extent in the interval of time considered, it should be remembered that any process other than one which keeps the quantity of free electricity in each element of volume zero will give rise to E.M.F.s tending to modify the current in such a way as to enable conduction to continue along the lines indicated.*

But, for the purposes of this note, it is both unnecessary and inadvisable to dwell upon the phenomena of polarisation, whether in the form of P.D.s within the solution or at the electrodes, which are inevitably present. Such considerations to be complete would have to take account, for example, of the fact that the ions of the solvent may also be involved. And, most of all, it has to be remembered that the diagram is only used in the many text-books in which it occurs, as a means of explaining Hittorf's method of finding the migration constant.* For this purpose the argument of §3 can be shown to be adequate by means of the following simple illustration of Hittorf's method.

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* A further reference to this point will be found, in the reply to the discussion on the Paper.

A glass tube of any convenient length and diameter is taken (quite a small tube will suffice), together with two corks through which pieces of stout copper wire are inserted centrally to act as electrodes. The tube is fixed in a vertical position with one of the corks fitted tightly into its lower end. The tube is nearly filled with a concentrated solution of copper sulphate; it adds to the instructiveness of the experiment if a saturated solution is used. The other cork, which is fitted rather loosely, is then inserted into the upper end, so that a centimetre or two of the wire which passes through it is immersed in the solution. A current from a two-volt accumulator is then passed through the solution for some hours, the lower wire being the anode and the upper the cathode. The colour of the solution round the cathode gradually disappears. The manner of the disappearance is significant.

It is easily seen that the loss of colour is not confined to the immediate neighbourhood of the wire but extends over the whole of the liquid above a horizontal plane lying near the lower end of the wire. The inferences from this are that convection currents are circulating continuously in the upper part of the tube, that one part after another of the liquid contained in this space comes into the region where the main portion of the current is flowing and that this liquid gets continuously poorer in copper sulphate because each part loses a fraction of its salt content as it moves over the electrode. There is, therefore, no difficulty in this case in seeing where the bulk of the additional molecules, required as in §3, is obtained.†

It may be interesting to add that, if a saturated solution has been used, crystals of copper sulphate can be observed round the anode at the conclusion of the experiment. These represent the "anode gain," just as the destruction of colour in the upper part of the tube represents the (equal) "cathode loss."

This experimental illustration can be made additionally instructive, from the point of view of this note, if a second tube of identical construction is arranged in series with the first. The two tubes are placed side by side and the upper electrode is the cathode in each. The solution in the second tube besides being saturated with copper sulphate contains (for example) an equivalent amount of zinc sulphate. By comparing the colours of the two cathode spaces (or the apparent colours of the electrodes as seen through the cathode liquids) from time to time after the current has begun, it becomes evident that the solution round the cathode in the second tube loses copper at the greater rate. In this tube the cationic stream consists partly of zinc ions and the amount of copper carried to the cathode per second by the current is therefore less than in the first tube. Hence, since the rate of deposition of copper on the two cathodes is the same, the solution round the cathode in the second tube has the greater demand made upon its supply of copper. The rates of loss will be, approximately, in the ratio $(v+\frac{1}{2}u) : v$, if we suppose the zinc and copper ions to be equally concentrated in the second tube, and to have approximately the same velocity.

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* Not necessarily giving $v/(u+v)$ if the ions are hydrated.

† Diffusion from below is, of course, never quite absent, and cases in which it is the only means of supply of the molecules required have, as is well known, been carefully studied.

I think experiments such as this remove any doubt about the need for distinguishing, among the ions deposited, between those ions which are carried by the potential gradient and those which are not.

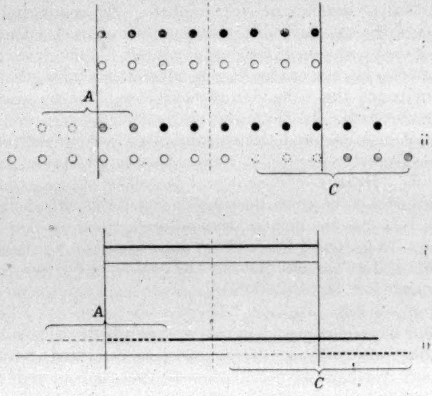
5. It has, of course, to be remembered that it is inadvisable to attempt to follow too minutely the motions of particular ions, for these, as well as the molecules out of which they come, have other motions besides those impressed by the applied electric field. The purpose of this note will, however, be attained if it shows how (subject to the limitations which any diagrammatic representation must contain) the picture usually given can be made more intelligible.

For this purpose it is only necessary to make the additions to Figs. 1 and 2 shown in Figs. 4 and 5 on p. 154.

The molecules contained within the bracket near C, in each figure, are those which actually disappear from the cathode space, while those contained within the bracket near A are those lost by the anode liquid. The ions to the right of C and to the left of A are those removed from the solution at the same time.

These diagrams show explicitly that ionised molecules of salt have to be fed into the current stream at the electrodes in order to keep it going, and it is just this essential feature of the phenomenon that the usual diagram omits.

6. It will be understood that Fig. 4 (or Fig. 5) is not intended to be more than a crude representation of any actual case.* For instance, the diagram contains no suggestion of the proportion which each electrode space (of variable concentration) bears to the total volume occupied by the electrolyte. The figure could be improved in this respect by replacing the median line by two parallel lines with a gap between them to represent the interior of the electrolyte. And, as a further improvement, the ions might be shown (or considered to be) less widely spaced in this link between the two electrode regions. For, in general, the concentrations N' and N'' (Fig. 3) must be less than N. If the current is to flow at a given rate for a finite interval, the rate of supply of fresh molecules to each electrode region must equal the rate of removal which the current involves. Diffusion is the only steady source of supply of these fresh molecules. Therefore the concentrations near the electrodes must always become definitely less than that in the interior of the electrolyte. The necessary differences of concentration could, however, be small if the current were not large



FIGS. 4 & 5.

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* Apart from the fact that in practice there is usually an anode gain instead of an anode loss.

and if, by gravitational convection or otherwise, the original concentration of the solution were maintained, as far as possible, along the whole path of the current. The concentration gradients near the electrodes (which determine the rates of supply of fresh molecules) could then be appreciable even when the actual differences of concentration, between the main solution and the electrode layers, were small.*

ABSTRACT.

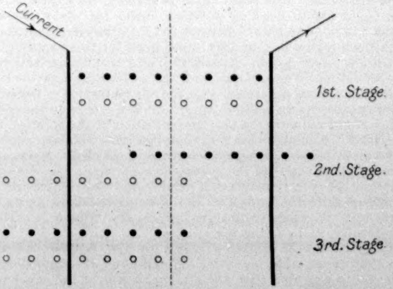
The object of this Note is to show how a familiar diagram, appearing in many text-books, can be improved in a way which makes it easier to appreciate what happens at the electrodes in the simpler examples of Hittorf's method of determining the migration constant. An attempt is made to give precision to an idea which is sometimes vaguely expressed and frequently ignored.

DISCUSSION.

Mr. D. Owen considered that the usual graphical method expressed the integral effect simply and satisfactorily unless pressed in detail. The analysis of paragraph three of the Paper, whilst adding precision to the conclusions, did not modify them or "explain" them. The fact of the existence of a volume distribution of electricity near to the electrodes implied an increased potential gradient which played a part in the actions occurring in those regions.

Dr. Willows suggested that, if Mr. Owen's view were correct, it should be possible to detect the potential gradients to which he referred.

Mr. F. E. Smith remarked that Dr. Smith's Paper dealt with a real difficulty, and one which teachers of electricity had to face. He remembered giving lectures on the subject to very elementary students, and, feeling dissatisfied with the explanatory diagrams in text-books, had adopted another form of explanation. In dealing with the phenomenon the negative ions were never said to be discharged. The general argument followed was to regard matter as being in four states—solid, liquid,



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* *See also* p. 156.

gaseous and ionic. It was already conceded from analogies that copper ions and metallic copper differed because of a difference of electrical energies. Conversion from one into another could be brought about by adding or subtracting electrical energy. Thus, in the electrolysis of copper sulphate solution with copper electrodes, the electrode at high potential lost energy by conversion of a part of itself into positive ions, and the negative electrode gained energy from the solution due to positive ions giving up their charge and being converted into the metallic form. Taking Dr. Smith's Fig. 1 of the Paper, the process of electrolysis would be explained by adding to it the third stage shown in the figure. The negative ions were never discharged. The copper ions put into solution from the positive electrode were associated with them, and are shown in the figure. The diagram shows (1) the changes of concentration at the two electrodes, (2) that the mean concentration of the electrolyte is unaltered, (3) it can be used to obtain the migration ratio.

Dr. Smith, in reply, said: In the original draft of the Note, as submitted to the Society, he had hazarded the opinion that perhaps the Authors, who used the diagram, wished it to be understood that the excess ions shown at the ends of the chains were removed by excess potential gradients. He had deleted this conjecture, and had substituted a footnote (which was, in fact, a quotation), because he had been unable to find any proof that this was the view taken. In any case it was unsatisfactory. Mr. Owen seemed to imagine that there was some virtue of simplicity about this view which made the analysis of §3 unnecessary. This was not the case. The problem was not simyly to state how a Hittorf migration experiment might be supposed to begin. It was as necessary to show clearly what occurred while it continued. This was the object of the Note. The analysis of §3 was merely a general method of expressing the fact that some of the ions which take part in the electrolytic process are fed into the circuit near the electrodes, and are not brought there by the potential gradients. Views which "explain" the facts, while ignoring this, have been the cause of needless confusion in the minds of students. The analysis of §3 showed, for example, that conduction could not proceed as it began unless for every $(u+v)$ cations deposited v cations and v anions were fed into the circuit at the cathode. If the cathode region had to draw upon itself for this supply of ions, the concentration there would rapidly fall and the "polarisation" at the cathode would rise in accordance with the well-known relation connecting the contact potential difference with the concentration. Diffusion, however, always played an essential part. When it was promoted by convection, a slight reduction in the concentration of the solution round the cathode would be enough to set up an appreciable diffusion current which would be maintained in the way described in §4 of the Note. This was the current which supplied the necessary molecules to the cathode space. The relation between this diffusion current and the electric current could be represented by the equation $kn=vi/(u+v)e$, where k is a diffusion constant, n is the concentration gradient at the cathode, i is the electric current density, and e is the ionic charge.

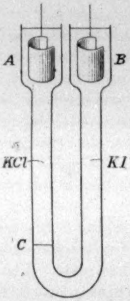
With regard to the question raised by Dr. Willows, he was of the opinion that measurable potential differences of the kind described did not exist. He was glad that the Chairman was of the same opinion as himself with respect to the diagrams and descriptions usually given.

XVI. *A Method of Exhibiting the Velocity of Iodine Ions in Solution.* By S. W. J. Smith, *M.A., D.Sc., F.R.S., Assistant Professor of Physics, Imperial College.*

Received March 9th.

I have shown the following experiment in lectures on electrolysis at the Imperial College for many years, since 1900 in fact; but have not described it hitherto.

It is of the same general kind as those first made by Sir Oliver Lodge, and subsequently by Whetham, Masson, Steele, Denison and others; but it will be seen, by those familiar with their work, that it has certain distinctive features of its own to which, perhaps, it is worth while to draw attention. I am led to offer the following account of the experiment by the reminder from the President, at the last meeting, that interesting experiments are always welcomed by the Society.



For the sake of brevity, I will confine myself to a description of the method of obtaining approximate results and omit the precautions which must be taken if great accuracy is desired.

The apparatus, in its simplest form, is represented in the diagram. The containing vessel is a U-tube with widened ends as shown. The diameter of the tube may be about 0·5 cm. or less. The cross-section of the tube should be fairly uniform and, in particular, should not be less at the bend than in the limbs. Either 25 cm. or 50 cm. is a convenient (total) length for the tube if it is desired to use it in connection with an ordinary lighting circuit voltage of 100, or thereabouts, and to obtain a rapid estimate of the velocity of the ions.

The electrodes (at A and B) are, preferably, of platinum foil. The liquids used are equally concentrated solutions, containing —*e.g.*, either 0·2 gm. or 0·1 gm. mol. per litre, of potassium chloride and potassium iodide respectively. The tube may be filled, in the way described by Whetham, by closing the end of the A limb while the B limb is filled and then closing B while the A limb is filled.

The novelty of the experiment lies in the method of exhibiting the line of separation between the solutions.

For this purpose a small quantity of mercuric chloride (corrosive sublimate) is dissolved along with the KCl. [In the endeavour to maintain symmetry an equal quantity of the same salt may be added to the KI.]

If, under these circumstances, the filling is carefully performed, a thin yellow disc of mercuric iodide, precipitated by the action of the KI upon the $HgCl_2$ contained by the KCl, will appear at the junction between the electrolytes. Even if the filling is performed rather carelessly, this disc soon becomes sharply defined because the mercuric iodide, although insoluble in KCl, dissolves in the KI and therefore cannot exist continuously except at the boundary between the two electrolytes.

When the line of separation has become well defined, the electrodes at A and B are connected to the source of supply, that at A being made the anode. The boundary at C immediately begins to move upwards. It travels as an extremely thin horizontal disc, which can be located very accurately and projected with ease. Moreover, under the conditions already mentioned, the disc will move at speeds of the order of 1 mm. per minute, so that its motion can be followed without difficulty by a large audience, and an approximate estimate of its velocity can be obtained in a few minutes.

To illustrate what happens, observations of the position of the disc, taken at intervals of 5 minutes for an hour after the E.M.F. was applied, are tabulated below. The potential gradient was about 3·7 volts per centimetre. The current was reversed, B being made the anode, after it had run for 30 minutes. The gradual rise in the velocity (shown in the difference column) is due to the rise in temperature of the electrolytes (and resulting increase in the mobility of the ions) as the experiment proceeds. For obvious reasons the rise in temperature is most rapid at the beginning of the experiment.

Mins.	Cm.	Diff.	Mins.	Cm.	Diff.
30	13·6		30	13·6	
		0·68			0·54
25	12·92		35	13·06	
		0·72			0·71
20	12·2		40	12·35	
		0·67			0·74
15	↑ 11·53		45	↓ 11·61	
		0·55			0·73
10	10·98		50	10·88	
		0·51			0·70
5	10·47		55	10·18	
		0·47			0·72
0	10·0		60	9·46	

The positions of the line of separation were determined by means of a millimetre scale placed alongside the tube.

The possibility of observing the reverse motion of the anions is due to the fact that the chlorine gas separated at A soon travels down the tube in sufficient quantity to decompose a fraction of the KI with separation of iodine. In consequence the solution below the disc soon becomes distinctly yellow. The coloration so produced permits observation of the retreat of the line of separation between the iodide and the chloride when B is made the anode.

Otherwise the rate of descent could not be measured over any considerable range, for, generally, the yellow disc of mercuric iodide disappears before very long when the current is reversed. This is no doubt due to the fact that when the iodine ions are moving downwards they are moving away from the mercuric chloride which can only reach them by diffusion (or by convection due to irregular heating). The summit of the yellow coloration, although not so easily determinable as that of the yellow disc, can, however, be fixed with fair accuracy, and so its velocity can be determined. It descends at the same rate as the iodine ions because, the solubility of iodine in KCl being negligibly small compared with its solubility in KI, the dissolved iodine retreats with the iodide.

The course of events being as indicated above, I may add the results of an attempt, made with the same apparatus on another occasion, to obtain an estimate of the velocity of the ions, at some definite temperature, in centimetres per second under a gradient of 1 volt per centimetre. The solutions (as in the previous case) contained 0·2 gm. mol. per litre. The current was allowed to run for about 20 minutes, in order to avoid the rapid rise in temperature at the beginning, before observations were begun. Similarly, the reversed current was allowed to run for some time before the second set of observations was made. The distance traversed by the line of separation during the first half hour of the experiment (measured by means of a small cathetometer) was 4·13 cm. The distance traversed in the second half hour was 4·53 cm. The difference was probably due mainly to a higher mean temperature in the second half of the experiment. On this occasion an ammeter was included in the circuit. The reading rose slowly during the observations. Its mean value during the hour was 0·03 ampere. The specific resistances of the electrolytes were measured at 10°C. (the temperature of the room) just before the tube was filled. The mean value was approximately 55 cm. ohms. The value of the current immediately after the circuit was completed was 0·023 ampere. The area of cross-section of the tube was about 0·31 sq. cm. Hence the initial potential gradient in the tube was approximately

$$(0{\cdot}023 \times 55)/0{\cdot}31 = 4{\cdot}1 \text{ volts per centimetre.}$$

Assuming the potential gradient to have remained constant throughout the experiment, the fact that the mean current was about 30 per cent. higher during the observations than at the first completion of the circuit means that the specific resistance of the electrolytes was about 30 per cent. less than its initial value at 10°C.—*i.e.*, that the average temperature of the electrolytes during the observations was about 25°C. Hence the velocity of the anions, iodine and chlorine, as determined in this way, is about

$$(4{\cdot}13 + 4{\cdot}53)/(3{,}600 \times 4{\cdot}1) = 0{\cdot}00059 \text{ at } 25^\circ\text{C.}$$

in cm. sec.$^{-1}$ per volt cm.$^{-1}$. But, of course, if accurate and not rapid determinations were required, much smaller potential gradients could be employed. The heating effects would, similarly, be less troublesome if more dilute solutions were used.

It may be noticed in connection with the method that solutions of KCl and KI of equal molecular concentration become electrochemically more nearly identical the more dilute they are. Even at moderate concentrations the conductivities are the same within a few per cent. Solutions of equivalent strength are, therefore, practically equally ionised, and the velocity of the iodine ions in the one is practically equal to that of the chlorine ions in the other. A consequence of this is that not only is the potential gradient the same in both solutions (if the tube is of uniform cross-section) but there is also no contact potential difference between them. These were the facts which led me to endeavour to find a simple method of fixing the line of separation between solutions of the salts in question.

Another device which can be used, and was the first that occurred to me, consists in adding a small quantity of silver nitrate to the KCl solution and re-dissolving the slight precipitate of silver chloride, which is formed, by the addition of a little ammonia. The upward movement of the iodine ions is now exhibited by the formation of silver iodide which is practically insoluble in ammonia. The progress of the ions is not as interesting to watch as in the case described above, because, the silver iodide not being soluble in the excess of KI, the point which the iodine ions have reached at any moment is not now represented by a thin disc but by the summit of the general cloudiness produced by the precipitated iodide of silver.

ABSTRACT.

Dilute solutions of potassium iodide and potassium chloride of equi-molecular concentration have almost the same electric conductivity. They are, therefore, of interest in connection with the direct measurement of ionic velocities. The Paper describes a simple method of observing their common boundary. For this purpose a little mercuric chloride is added to the potassium chloride solution. An extremely thin layer of mercuric iodide then forms where the two solutions meet. The method is particularly convenient for lecture purposes, and an approximate value of the ionic velocity can be obtained in a few minutes.

The Paper gives examples of the use of the method. The current is first passed in the direction which causes the iodine ions to travel towards the chloride. The chlorine liberated at the anode in this case supplies a means of re-determining the velocity of the ions when, the current being reversed, they move in the opposite direction.

XVII. *The Electrical Capacity of Gold-leaf Electroscopes.* By T. Barratt, *D.Sc., A.R.C.S.*

Received March 20, 1916.

I. Introduction and Historical.

The modern gold-leaf electroscope has for some considerable time been employed by workers in radioactivity as an instrument of precision comparable with that of other instruments used in electrical measurements. Many workers in other branches of physics, however, still appear to regard the instrument as of merely historical interest. It is the experience of the author that with the help of the gold-leaf electroscope measurement of potential can be made with an accuracy of, at any rate, 1 per cent. between, say, 50 and 300 volts, the limits depending on the particular instrument. The gold-leaf electroscope possesses many advantages over the usual type of electrometer. The latter is exceedingly troublesome to set up and to work, and requires very great care in maintaining satisfactory insulation. Its capacity is many times that of the electroscope, which can, therefore, measure much smaller currents. [*See* Paper by G. W. C. Kaye, Phys. Soc. "Proc.," 23, p. 209, 1911.] In addition, the electroscope is much cheaper, takes up very little space, is easily transported and can be used in any position.

Methods for the determination of the capacity of the gold-leaf electroscope have been given by F. Harms* and by Lichtenecker.† In the measurement of such small capacities the usual commutator methods cannot be employed. Accurate and well-insulated standard condensers of the same order of capacity as that of the electroscope cannot be obtained; and, again, the capacity of any connecting wires, switches, &c., are of the same order of magnitude as that of the leaf system itself, and are not known with any degree of accuracy. In order to overcome the latter difficulty, Harms‡ allowed drops of mercury, alcohol or water to fall from a charged capillary tube into an ionisation vessel connected with the electroscope. Obviously the method cannot be employed with an electroscope not possessing such an ionisation vessel. An experiment often took 18 minutes to perform, and corrections had to be made for loss of potential during that time. It would also appear that a further correction was necessary for electrical energy produced by the fall of the drops of liquid from a great height (over 100 cm.). Lichtenecker* attached a sphere to the electroscope by a long wire, and by measuring the capacity of the electroscope, sphere and wire for various lengths of the wire deduced the capacity of the electroscope alone. In both of these methods elaborate apparatus was necessary, and the individual results differed in some cases by as much as 10 per cent.

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* "Phys. Zeit.," 5, p. 47, 1904; "Ann. d. Physik," 10, p. 816, March, 1903.

† "Phys. Zeit.," p. 516, 1912.

‡ "Phys. Zeit.," 5, p. 47, 1904; "Ann. d. Physik.," 10, p. 816, March, 1903.

The method that appears to be generally used in the laboratory is to charge the electroscope to a known potential, allow it to share its charge with a small sphere of a few cms. diameter, and deduce the capacity of the electroscope from the observed drop of potential. Unfortunately, however, the capacity of the electroscope when in contact with the sphere is very different from its true capacity, and Harms† remarks that results differing by 25 per cent. will be obtained by this method. For example, the joint capacity of two spheres in contact, each of radius a, is not $2a$, but $2a \times \log 2$.‡ If the spheres are of radii a and b, and if b/a is large, the capacity of the smaller sphere is not a, but $\frac{a^2}{b} \cdot \frac{\pi^2}{6}$.

It is impossible, however, to obtain a similar formula for the combined capacity of a sphere and a conductor of such a shape as the rod and leaf of a gold-leaf electroscope.

II. Apparatus and Method of Experiment.

Preliminary experiments showed that the use of a parallel-plate air condenser in place of a sphere overcame this difficulty. There is nothing new in the method except in some of its details. For example, contact is made between condenser and electroscope, not once, but if necessary several times, the electroscope being earthed each time after contact. A long thin copper wire (gauge 30) is attached to the insulated plate of the condenser, which consists of plate glass covered with thin tinfoil (the two sheets of tinfoil facing each other), and insulated by three pieces of sulphur, whose thickness is accurately measured by a micrometer screw gauge. If the sulphur be scraped by a sharp penknife its insulating powers are almost perfect. The condenser is surrounded by a guard ring, so that its capacity is known with accuracy. In the present series of experiments a second condenser (without a guard ring) was used, its capacity having been first carefully compared with that of the guard-ring condenser. The capacity included that of the attached copper wire. It was found that the reading of the leaf of the electroscope was very nearly the same when joined to the condenser by the connecting wire as when the latter was disconnected and earthed. The fact that nearly all the lines of force of the condenser are crowded between the plates no doubt accounts for this.

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* "Phys. Zeit.," p. 516, 1912.

† "Phys. Zeit.," 5, p. 47, 1904; "Ann. d. Physik.," 10, p. 816, March, 1903.

‡ J. J. Thomson, "Elemts. of Elec. and Mag.," 3rd edition, p. 181.

The necessary small correction for the difference between the capacity of the electroscope as obtained by the above method and its true capacity (*i.e.*, its capacity when the usual conductors in the vicinity of the leaf system are all earthed) is easily obtained. It is found by experiment that the potential, as indicated by the position of the leaf, is slightly reduced when the attached wire from the condenser is disconnected and earthed. The percentage reduction is found to be the same, within errors of experiment, for all values of the potential. It varies slightly for different electroscopes, but is never more than about 2 per cent. If the potential is reduced from V to V' on removing and earthing the wire, then, as the charge on the leaf system is unaltered, the capacity is changed from C to C', where $C'V'=CV$, or true capacity $C'=CV/V'$.

For example, in the case of the electroscope examined in Section III. (i.), $V=300$, $V'=294$, $C=7{\cdot}13$.

Hence, true capacity$=390\times 7{\cdot}13/294=7{\cdot}27$ cm.

The electroscope and reading microscope were firmly secured to a rigid bench. A vernier attached to the microscope, and reading to one-twentieth of a millimeter, moved along a horizontal scale, and the reading of the leaf was obtained at potentials of 20, 40, 60, . . . 300 volts, as given by a battery of small accumulators, standardised by a voltmeter. A curve was then drawn connecting potential of leaf and reading of microscope scale. Such a curve is given in Fig. 1.

The battery, which has proved exceedingly satisfactory, was made in the laboratory at a very small cost. The cells were arranged in rows of 10, and could all be charged together by about 12 or 13 accumulators of the usual laboratory type.

The electroscope and condenser were connected and charged by means of an ebonite rod to a known potential, given by the reading on the scale and by reference to the curve. The wire from the condenser was disconnected from the electroscope with the help of a rod of sulphur, and the electroscope earthed by means of a copper wire soldered to the gas pipes. The condenser was again connected to the electroscope, disconnected, and the electroscope earthed. This process of alternate earthing of the electroscope and sharing the charge of the condenser was repeated as many times as necessary, and the capacity of the electroscope deduced. It is to be observed that the connecting wire does not form a part of the capacity to be measured, but is included in that of the condenser. The experiment takes only a few seconds, so that no correction is necessary for loss of charge.

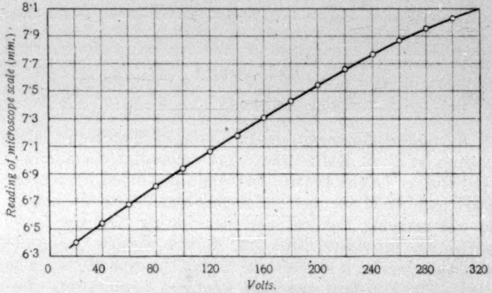

Fig. 1.—Curve Connecting Potential of Leaf and Reading on Microscope Scale.

If V is the original potential of the condenser and C its capacity, v_n the final potential of the system after n alternate earthings and re-chargings as above, and c the required capacity of the electroscope, it can easily be deduced that

$$v_n = \left(\frac{C}{C+c}\right)^n . V,$$

or

$$\log(C+c) = \log C + \frac{1}{n}(\log V - \log v_n).$$

III. Determinations of Capacity.

1. *Cubical Lead Electroscope.*—The edge of the electroscope was of length 20 cm. A central copper rod, length 18 cm.,

passing through sulphur in a glass cylinder 5 cm. long, 1·5 cm. diameter, carried a leaf 4·5 cm. long, 1 mm. wide.

TABLE I.

Dimensions of plates of air condenser: 35 cm. × 24 cm.; distance apart, 0·480 cm. Capacity of condenser and wire = 144 cm. Correction for obtaining "true capacity" = 2 per cent. [*See* Section II.]

First potential, V.	Second potential, v_n.	No. of charges n.	Capacity c of electroscope.	True capacity c' of electroscope.
100 volts	79 volts	5	6·95 cm.	7·09 cm.
100 ,,	62·5 ,,	10	6·93 ,,	7·07 ,,
100 ,,	49·5 ,,	15	6·91 ,,	7·05 ,,
150 ,,	118·0 ,,	5	7·10 ,,	7·24 ,,
150 ,,	92·5 ,,	10	7·13 ,,	7·27 ,,
150 ,,	73·0 ,,	15	7·08 ,,	7·22 ,,
200 ,,	122·0 ,,	10	7·29 ,,	7·43 ,,
250 ,,	153·0 ,,	10	7·24 ,,	7·38 ,,
300 ,,	185·0 ,,	10	7·13 ,,	7·27 ,,

2. *Emanation Electroscope.*—By Cook, of Manchester, after a pattern by Sir E. Rutherford. The emanation chamber was cylindrical, of height 14 cm., and was surrounded by a cylindrical chamber of the same diameter and 9·2 cm. in height. The rod carrying the leaf and penetrating also the lower chamber was provided with a disc of 5 cm. diameter, opposite which was a similar movable disc, so that the capacity could be varied. The leaf itself was 5 cm. long and 3 mm. wide. The results given in Table II. were obtained with the discs at their maximum distance apart.

TABLE II.

Capacity of condenser and wire = 144 cm. Correction for obtaining true capacity = 1·5 per cent.

First potential, V.	Second potential, v_n.	No. of charges n.	Capacity c of electroscope.	True capacity c' of electroscope.
240 volts	202·5 volts	3	8·39 cm.	8·51 cm.
280 ,,	249·5 ,,	2	8·55 ,,	8·68 ,,
280 ,,	235·5 ,,	3	8·55 ,,	8·68 ,,
280 ,,	222·5 ,,	4	8·52 ,,	8·65 ,,
280 ,,	210·0 ,,	5	8·53 ,,	8·66 ,,

With the movable disc as near as possible to the fixed disc, the capacity was increased in the ratio of 1·24 : 1.

[In this electroscope (kindly lent by Mr. F. H. Glew) the rod carrying the leaf had a backward slope, so that at about 150 volts the leaf remained very nearly in contact with the rod.]

3. *Small Cubical Lead Electroscope.*—This electroscope, of 10 cm. edge, was insulated by a sulphur bead *inside* the instrument, and charged by means of a metal charger, C (Fig. 3). This charger was well insulated by sulphur at S, and was of total length 13 cm. The rod carrying the leaf was 6 cm. long and the leaf itself was 4 cm. in length and 1 mm. wide. The joint capacity of leaf system ($=c$) and charger ($=c'$) was first determined in the usual way. Then the capacity (c') of the charger alone was measured as follows: The condenser, leaf system and charger were raised to potential V as given by the deflection of the leaf. The condenser was disconnected and leaf and charger earthed. The charger was disconnected from the leaf system, charged from condenser and earthed n times. Finally, all three were connected again, and their final potential, v_n, observed. Under these circumstances it can be calculated that

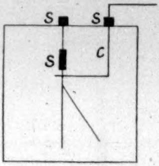

FIG. 2.—ELECTROSCOPE WITH CHARGER C.
S S S = Sulphur Insulation.

$$ {}_n v = \frac{C^n}{(C+\overline{c+c'})(C+c')^{n-1}} \cdot V, $$

$$ \text{or} \log (C+c') = \frac{1}{n-1}\{n \log C + \log V - \log (C+\overline{c+c'}) - \log v_n\}, $$

from which c', the capacity of the charger alone can be obtained. The results of the determinations are given in Table III.

TABLE III.

Correction for obtaining "true capacity" = 2·2 per cent.

(*a*) *Capacity of Leaf System and "Charger."*

First potential, *V*.	Second potential *v*.	No. of charges.	Capacity of leaf charger (*c*).	True capacity (*c′*).
300 volts	242·5 volts	10	3·80 cm.	3·17 cm.

(*b*) *Capacity of "Charger" alone.*

First potential.	Second potential.	No. of charges.	Capacity of "charger."	True capacity of "charger."
300 volts	256 volts	10	2·22 cm.	2·27 cm

(*c*) Hence, *true capacity of leaf system alone* = 3·17 − 2·27 = 0·90 cm.

4. *Ionisation Vessel and Gold-leaf Electroscope.*—The electroscope examined in Section III. (1) was connected with an "ionisation vessel," *V* (Fig. 3). This vessel was of cubical form, of edge about 16 cm. A radioactive substance (uranium oxide) could be placed on a square plate, *A*, of area 64 sq. cm., and a similar plate, *B*, parallel with *A*, was connected to the leaf system of the electroscope *E*.

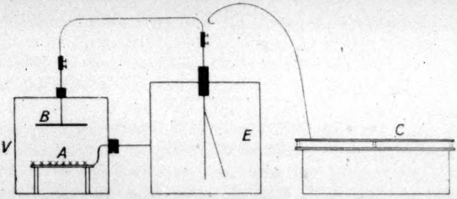

FIG. 3.

V = Ionisation vessel. E = Electroscope. C = Condenser.

A common method of measuring the capacity of a system including an "ionisation vessel" and electrometer is to observe the rate of fall of potential (as given by the electrometer) due to the ionisation produced between two parallel plates, *A* and *B*, (*a*) when connected with a condenser of known capacity, (*b*) when the condenser is disconnected.

In order to compare this method with the one described in the present Paper the capacity of the system was determined by both methods.

If *C* is the capacity of the condenser, and *c* that of the ionisation vessel and electrometer, *T* and *t* the times taken for a given fall of potential with the condenser (*a*) connected, (*b*) disconnected ; then

$$\frac{C+c}{c}=\frac{T}{t}, \text{ or } c=\frac{Ct}{T-t}.$$

Capacity of Ionisation Vessel and Electroscope.—(1) By measuring rate of fall of potential due to uranium oxide. Potential fell from 300 volts to 211 volts, (*a*) with condenser of capacity 144 cm., in 505 seconds ; (*b*) without condenser, in 58 seconds.

First potential, V.	Second potential, v.	Time with condenser, T.	Time without condenser, t.
300 volts	211 volts	505 secs.	58·0 secs.
300 „	187 „	624 „	71·5 „

The values for the capacity from these observations are 18·68 cm. and 18·31 cm. respectively ; or, when correction (0·9 per cent.) is made for earthing wire from condenser, 18·85 cm. and 18·47 cm. respectively.

(2) By the method of this Paper.

First potential, V.	Second potential, v.	No. of charges.	Capacity, c.	True capacity, c'.
300 volts	208 volts	3	18·70 cm.	18·87 cm.
300 „	185 „	4	18·50 „	18·67 „

Satisfactory agreement is thus obtained in the results given by the two methods.

IV. Discussion of Results.

The consistency of the results enumerated in Section III. may appear somewhat surprising to one not acquainted with the possibilities of a modern gold-leaf electroscope. If proper precautions be taken, a particular experiment can be repeated again and again with practically the same result, and the conditions can be widely varied without much alteration in the final value obtained for the capacity of the electroscope. The divergence of the leaf appears to have very little effect on the capacity of the system as a whole, except, perhaps, when the leaf is nearly in contact with the rod supporting it, in which case the capacity would appear to be slightly lower. This may, however, be due to a decrease in sensitiveness with the leaf in such a position, though Harms* obtained in some cases a similar result. It is worthy of notice that the comparatively large capacity of the standard condenser employed—which would be a serious drawback in other methods—presents no difficulty in the method of the present Paper, provided that contact be made between condenser and leaf system a sufficient number of times. With such small capacities as those dealt with here very small ionisation currents can be accurately measured. For example, in the case of the electroscope of capacity 0·90 cm., the ionisation within the vessel reduced the potential from 300 to 280 volts (corresponding to 20 divisions of the microscope scale) in about an hour. This corresponds to a current of approximately $1{\cdot}6\times10^{-13}$ ampere.

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* Loc. cit.

V. SUMMARY.

The capacities of gold-leaf electroscopes of various patterns have been determined by a method which depends upon obtaining the relation between the divergence of the leaf and the potential applied to it, and the observation of the fall of potential of the leaf system when it shares its charge a convenient number of times with a standard parallel plate air condenser. It is found that the capacity is practically independent of the amount of divergence of the leaf, except when this divergence is very small, in which case the capacity becomes slightly lower. Ionisation currents of the order 10^{-13} ampere can be accurately measured by an electroscope of capacity about 1 cm. For some purposes the gold-leaf electroscope possesses marked advantages over the quadrant electrometer. The method employed was found to give satisfactory agreement with the results obtained by another method.

ABSTRACT.

A gold-leaf electroscope is frequently used to compare exceedingly small ionisation currents. For this purpose it is much more sensitive than a quadrant electrometer. If the capacity of the electroscope is known then the absolute value in amperes of the ionisation current can be deduced. A method is described for measuring the capacity of a gold-leaf electroscope, the method depending on sharing the charge of a parallel plate air condenser of measurable capacity as many times as necessary, and deducing the capacity of the electroscope from the observed drop of potential. The method gives consistent results when the experimental conditions are widely varied. The amount of deflection of the leaf appears to have little influence on the result.

DISCUSSION.

Mr. A. CAMPBELL: The consistency of Dr. Barratt's results shows that the modern gold-leaf electroscope is an instrument of precision and justifies the use of the simple method of divided charge for measuring its capacity. The method, however, tends to make the capacity seem more constant at different readings than it really is. When a plate condenser without a guard-ring is used, the edge correction can be obtained by Kirchhoff's formula.* But standard variable air condensers marked in micro-microfarads from about 30 up to 200 are now to be had in this country, and form very convenient standards of small capacity. The capacities of ordinary electrostatic voltmeters are not very high, that of a 100-volt Kelvin or Ayrton-Mather instrument being of the order of 70 micro-microfarads. Their large variation with the reading shows that, unlike the gold-leaf type, these instruments have very little ineffective capacity. For the measurement of small capacities the Carey Foster method seems the most convenient, and it gives the power factor at the same time. With 20 volts on the condenser at a frequency of 800 ∿ per second, a capacity of 5 micro-microfarads can be measured with an accuracy of about 1 per cent. It is a pity that the author gives his results in mixed units, the voltages being in electromagnetic units (volts) and the capacities in electrostatic units ; this can only lead to confusion. The practical system of volts, amperes, coulombs, farads, &c., is sufficient for all actual measurements.

Capt. C. E. S. PHILLIPS observed that the experiments in which the capacity of a system containing an ionisation vessel was compared by two methods showed that the capacity of a condenser with ionised air between the plates was not different from its capacity with unionised air as dielectric.

Prof. G. W. O. HOWE suggested that the reason the capacity of the electroscope was uninfluenced by the vicinity of the charged wire from the condenser was that the capacity of the wire was small ; it had nothing to do with the lines of force of the condenser.

Dr. BARRATT : The edge effect in the condenser used was very small, as the plates were each of area 840 sq. cm. and only 0·48 cm. apart. This was, however, allowed for by comparison with a guard-ring air condenser. The capacity of most gold-leaf electroscopes is of the order of 1 micro-microfarad—*i.e.*, only 1/50 to 1/100 of that mentioned by Mr. Campbell. The air condensers which Mr. Campbell describes are of capacity 50 to 200 times that to be measured, which would be a great objection in other methods than that in the Paper. Carey Foster's method appears to become less accurate as the capacity to be measured approaches those dealt with in the present research. The apparatus, again, is more costly and less simple. The mixing of the units was due to the fact that the measurements were simply put down in the particular system of units employed in each measurement. Prof. Howe's alternative explanation of the want of effect of the charged wire appeared to be only another way of expressing the same fact. In the case of a charged sphere in contact with the electroscope the capacity of the latter is influenced by the lines of force radiating from the sphere, while in the case of the condenser the connecting wire is of comparatively small capacity, and is connected, therefore, with fewer lines of force.

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* Berlin "Akad. Monatsberichte," p. 144, 1877.

XVIII.—*The Laws of Variation of Resistance with Voltage at a Rectifying Contact of Two Solid Conductors, with Applications to the Electric Wave Detector.* *By* D. OWEN, *B.A., B.Sc., Birkbeck College, London.*

RECEIVED MARCH 20, 1916.

VARIOUS theories have been put forward to account for the rectifying action at a contact such, for example, as that between zincite and chalcopyrite, to which an alternating voltage is applied. It is not necessary to refer to more than two, which alone have up to the present claimed serious consideration. Both before and since Dunwoody's application of the mineral detector to wireless telegraphy, it was recognised that certain minerals possess extraordinarily large thermoelectric powers, exceeding in some instances by ten times or more that between bismuth and antimony. A natural explanation in terms of thermoelectric action thus lay to hand, which appeared all the more probable from the fact that these minerals also possess a large negative temperature coefficient of resistance.

In 1907, however. appeared a Paper by Prof. G. W. Pierce, containing an account of experiments which were regarded as precluding such an explanation, the main ground for this conclusion being the undoubted fact that the direction of flow of the rectified current across a junction is generally (in the case of mineral contacts) contrary to that of the current set up on heating the same junction.

A theory—since known as the electronic valve theory—was thrown out in that Paper, according to which we have in certain minerals a new phenomenon, namely, the easy passage of free electrons in one direction across the contact, but not in the contrary direction. This is the second view which has held the field.

The thermoelectric explanation has been developed by Dr. W. Eccles, who in 1913 expressed it in mathematical form, and showed the concordance of this theory with many of the observed phenomena.

On the other hand, despite the attraction which the free electronic view has possessed for many writers, little, if anything, has been done to establish definite laws answering to that view; and this tempting hypothesis has not advanced beyond the stage of mere speculation.

Most workers on this subject have directed their attention to the determination of the current characteristic, both current and voltage being directly measured. This method has several defects: it involves the application of the voltage for a comparatively long interval of time; again it is least accurate where the results are of the greatest interest, namely, at very small voltages. Current characteristics are usually taken with applied voltages up to or beyond 1 volt, and some workers have extended the range up to 20 volts. The minimum voltage which is necessary to produce a signal in the receiving circuit of a wireless station is probably only of the order of a hundredth of a volt.

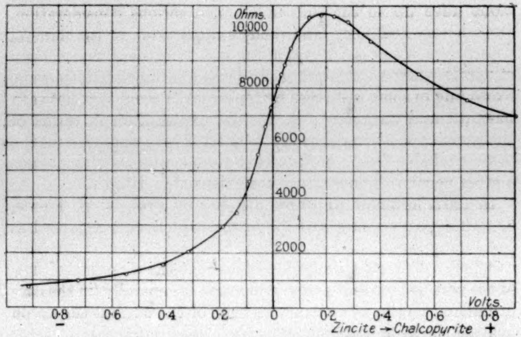

FIG. 1.—RESISTANCE CHARACTERISTIC OF A ZINCITE-CHALCOPYRITE CONTACT.

The present Paper deals with measurements of the resistance of the contact. The primary aim was to examine to what extent the resistance-characteristic expresses the nature of the physical actions occurring, and to obtain data leading to a discrimination between the hypotheses referred to.

Preliminary measurements showed that with care to avoid mechanical disturbance, and provided time was allowed for the contact to "settle down"—a process sometimes occupying minutes, sometimes hours—the resistance was sufficiently definite and reliable to permit of the application of the Wheatstone bridge, with all the power and flexibility of this method of attack.

The characteristic obtained with a zincite-chalcopyrite contact is shown in Fig. 1.

This type was followed by all the mineral combinations tried. The main points of interest are as follows: When a small voltage is applied the resistance rises, falling at the same rate when the voltage is reversed; a maximum occurs on the side of initial increase; at the higher voltages the characteristic is a falling one, the gradient diminishes on either side, positive or negative. Let

v=voltage applied across the contact.
R_0=resistance when v is zero.
R_m=maximum value of resistance, occurring at voltage v_m.

Investigation of a great number of contacts has led to the following quantitative results:—

1. At $v=0$ the gradient of the resistance characteristic is proportional to the limiting resistance R_0, that is, $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$ is a constant for a given pair of materials. This quantity, which is analogous to the temperature coefficient of resistance, may be termed the voltage coefficient of the contact;

2. v_m is independent of R_0;

3. The ratio R_m/R_0 is independent of R_0. When a series of characteristics are obtained from contacts of widely varying resistance or area of contact, and the ordinates of each reduced in the ratio $1 : R_0$, the resulting curves are found to coincide, yielding what may be called the *specific characteristic* of the given pair of substances (Figs. 2 and 10).

The above results are found to conform to an expression connecting R and v derived on the basis that the phenomena are thermoelectric.

A series of experiments was carried out on a number of contacts both elements of which were metallic, and for which the thermoelectric and other relevant constants are known. These confirm the same view.

The facts as to the sign of the rectified current will be shown on close examination to be, not in opposition, but in simple accordance with the thermoelectric explanation.

The experimental results above outlined form the basis of a calculation of the conditions of best sensibility in a wireless receiving circuit, with or without a polarising voltage. Similar considerations determine the sensitiveness to be expected in a combination of rectifying contact and direct-current galvanometer, as applied to the detection of small alternating voltages in bridge or other null methods of measurement.

I. *Experimental Details.*

The contacts tested were found to range in resistance from fractions of an ohm in the case of metallic combinations to millions of ohms in the case of zincite or carborundum contacts. The Wheatstone bridge was employed throughout. The applied voltage was varied from a millivolt or less up to 1 or 2 volts, the value being read on a multiple-range millivoltmeter in shunt with the bridge. If P and Q denote the ratio arm resistances, S that of the variable arm, V the voltage across the bridge, then the voltage v applied to the contact, and its apparent resistance R are calculated from the formulæ,

$$v=\frac{P}{P+Q}\,.\,V, \text{ and } R=\frac{P}{Q}\,.\,S.$$

The current through the contact is, of course, given by the expression v/R.

The two elements of the contact were—in the case of minerals—soldered by means of Wood's fusible metal into copper cups hard-soldered on to copper plates. In order to damp mechanical vibration the contact was mounted on a thick pad of cotton wool. A simple lever arrangement permitted of continuous adjustment of the mechanical pressure at the contact. Non-rigid electrical connection was obtained by the use of mercury cups wherever necessary.

The effect of time of application of the voltage was found to be considerable at the higher voltages. By limiting the duration of the testing current the measured resistance becomes quite determinate. Small periods of contact were obtained by aid of a metallic ball or ring suspended by a fine wire which also served as battery lead. On pulling out by a fine thread, then letting go, the ball was made to strike a heavy metal plate, thus making the circuit for the period of collision, which was determined in a separate experiment. Many of the measurements recorded were taken with a contact lasting 0·003 second. In order to secure the requisite sensibility under these conditions a Broca galvanometer of 1,000 ohms resistance was used.

In all the measurements the galvanometer key was kept closed, the resistance in the variable arm of the bridge being adjusted to give balance on closing the battery circuit.

The sign of the thermo E.M.F. was found for each contact in situ, the small rise of temperature required being obtained without any disturbance of the contact by applying a flame momentarily to a thick copper wire attached to the plate which supported the contact.

II. *The Experiments on Minerals.*

The mineral contacts tested were the following :—

Zincite-platinum.
Zincite-chalcopyrite.
Carborundum-platinum.
Galena-platinum.
Chalcopyrite-platinum.
Bornite-platinum.
Chalcopyrite-bornite.

It was considered desirable from the point of view of simplicity and reproducibility to use a metal as an element of the contact. Platinum was chosen on account of its unoxidisability and high melting point.

Zincite.—Early observations showed that remarkably steady resistances were obtainable with the zincite-chalcopyrite combination. Thus, tests were conducted on the same contact at intervals extending over a week without any variation of the limiting resistance greater than 5 per cent. After a series of measurements over a range up to 1 volt, lasting about an hour and a half, the initial resistance was reproduced often to within a few parts in a thousand. To secure such constancy it is necessary to avoid excessive voltages—say, more than 1·5 volt—or at all events to apply them for only a small fraction of a second.

The following example of readings refers to the test from which the resistance characteristic of Fig. 1 was drawn.

TABLE I.—*Zincite-Chalcopyrite.*
$P=1{,}000$, $Q=100$.

v	R	Direction of current.	v	R	Direction of current.
0·0045	7,490	Zinc—>Chalc	0·0045	7,300	Chalc—>Zincite
0·0236	8,170	,,	0·091	4,620	,,
0·0463	8,910	,,	0·136	3,520	,,
0·0682	9,530	,,	0·182	3,000	,,
0·091	10,030	,,	0·227	2,600	,,
0·136	10,650	,,	0·318	2,100	,,
0·186	10,750	,,	0·409	1,640	,,
0·232	10,680	,,	0·545	1,300	,,
0·0045	7,500	,,	0·727	1·040	,,
0·282	10,500	,,	0·910	830	,,
0·364	9,800	,,	0·0045	7,350	,,
0·545	8,650	,,	...	...	...
0·727	7,700	,,	...	...	...
0·91	7,100	,,	...	...	...
0·0045	7,600	,,	...	...	...

Ten different contact points were taken in succession between the same pair of mounted minerals, and sets of readings taken from which the resistance characteristics were plotted. The limiting resistances were found to vary from a few thousands to a few millions of ohms. The contacts were chosen so as to give values of resistance approximately equispaced over the whole range, otherwise no selection was exercised. Variation of the mechanical pressure serves conveniently to secure the above adjustment. The highest value used was 540,000 ohms, since for higher values the diminishing sensibility of the bridge becomes unfavourable to accuracy at the lowest voltages. The following table summarises the results of the series :—

TABLE II.—*Series of Contacts Between Zincite and Chalcopyrite.*

No.	R_0	Rm	Rm/R_0	vm	$(dR/dv)_0$	$\left(\frac{1}{R}\frac{dR}{dv}\right)_0$
1	6,480	10,100	1·50	0·17	27,700	6·70
2	7,360	10,800	1·47	0·18	32,800	4·40
3	20,340	30,600	1·47	0·17	113,800	5·07
[4	24,000	28,100	1·17	0·30	39,500	1·64]
5	57,200	83,000	1·45	0·15	296,000	5·17
6	77,200	104,200	1·35	0·12	405,000	5·24
7	80,800	132,000	1·63	0·16	591,000	7·32
8	123,000	202,500	1·62	0·14	925,000	7·40
9	251,500	445,000	1·77	0·18	$2·18 \times 10^6$	8·70
10	540,000	855,000	1·58	0·11	$4·1 \times 10^6$	7·6
			Mean =1·54	Mean =0·15		Mean =6·40

$(dR/dv)_0$ is in every case found to be positive for current from zincite to chalcopyrite across the contact. With the exception of No. 4 (which was excluded in calculating mean values), it will be seen that the variations in the three quantities v_m, R_m/R_0 and $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$ are insignificant compared with the range of resistance covered by the series. When the *a priori* probability of lack of homogeneity in the material is considered, the variation of individual results from the mean for the nine contacts is surprisingly small. It seems safe to conclude that the essential action at the contact is expressed in the statement that $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$, *$R_m/R_0$, and v_m are dependent only on the materials constituting the contact, and not on the area or resistance of the contact itself.*

An examination of the curves indicates that at every point (unless v is large) the ratio R/R_0 is independent of the value of R_0. The graphs were reduced in scale so as to make R_0 unity in each case. The specific characteristics thus obtained for the zincite-chalcopyrite and other mineral contacts are shown in Fig. 2.

Galena.—A similar series of measurements was undertaken on contacts between platinum and galena. The specific resistance of the latter is much smaller than that of zincite, so that very small mechanical pressure at the contact must be used in order to secure even moderately high values of the resistance. A platinum wire of No. 24 S.W.G. was found suitable. The pressure was supplied by the spring action of this wire, or rather of a copper wire which terminated in a short length of the platinum wire. It is not easy to work with these light contacts, and much time and care were necessary to secure a satisfactory set of readings. Ten contacts were examined, the lowest being 34·1 ohms and the highest 1,400 ohms. Attempts at measurement on still higher values, a finer platinum wire being substituted, were abandoned as hopeless.

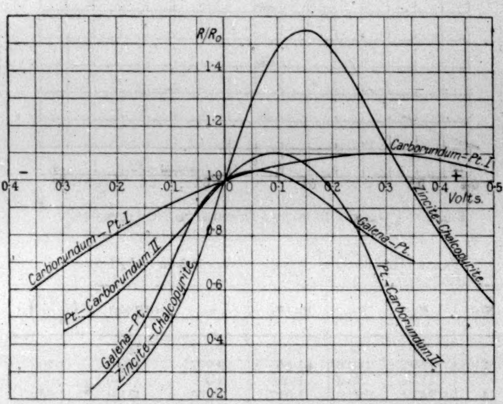

FIG. 2.—SPECIFIC RESISTANCE-CHARACTERISTICS OF SOME MINERAL CONTACTS.

One specimen curve is given in Fig. 3. The summarised results are contained in Table III.

$(dR/dv)_0$ is in every case positive when the current crosses the contact from galena to platinum. The conclusion to be

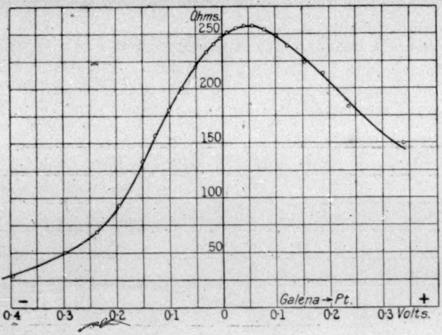

Fig. 3.—A Galena-Platinum Resistance Characteristic.

Table III.—*Series of Contacts between Galena and Platinum.*

No.	R_0.	Rm.	Rm/R_0.	vm.	$(dR/dv)_0$.	$\left(\frac{1}{R}\frac{dR}{dv}\right)_0$.
1	34·1	34·5	1·012	0·061	15·5	0·45
2	116·7	140·0	1·05	0·077	140·0	1·20
3	132·8	139·2	1·048	0·066	172·5	1·30
4	247·4	258·0	1·047	0·055	411·0	1·66
5	299·0	308·0	1·027	0·060	365·0	1·22
6	440·0	454·0	1·032	0·067	322·0	0·73
7	570·0	593·0	1·04	0·068	503·0	0·88
8	750·0	781·0	1·04	0·072	1,200·0	1·60
9	1,305·0	1,390·0	1·065	0·067	2,320·0	1·78
10	1,368·0	1,436·0	1·056	0·070	1,650·0	1·20
			Mean =1·042	Mean =0·066		Mean =1·20

drawn is again that the quantities $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$, v_m, and R_m/R_0 are independent of the limiting resistance of the contact. The voltage coefficient is about one-fifth the value of the same quantity for zincite-chalcopyrite.

Carborundum.—A contact of this material exhibits the same general behaviour, as is shown in the specimen curve of Fig. 4. Seven contacts were investigated, five on one specimen, which consisted of a conglomerate of small crystals (Series C), and

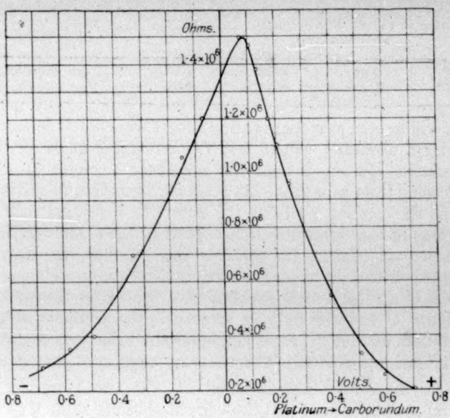

FIG. 4.—A HIGH-RESISTANCE PLATINUM-CARBORUNDUM CHARACTERISTIC.

two on another specimen, bounded by a large facet of crystal (Series C′). The resistances of contacts over the latter were never less than two million ohms, even under mechanical pressure as great as a kilogram weight.

TABLE IV.—*Carborundum-Platinum Contacts.*
Series C :—

No.	R_0.	R_m.	R_m/R_0.	v_m.	$(dR/dv)_0$.	$\left(\frac{1}{R}\frac{dR}{dv}\right)_0$.	Direction of current for $\left(\frac{dR}{dv}\right)_0$ positive.
1	460	510·5	1·11	0·28	370	0·86	Carb. to plat.
2	525	590·0	1·12	0·26	550	1·05	,, ,,
3	612	680·0	1·11	0·30	401	0·65	,, ,,
4	923	953·0	1·04	0·30	206	0·22	,, ,,
5	198,000	225,000	1·14	0·16	562,500	2·81	Plat. to carb.
Series C′ :—							
1	$1{\cdot}34\times10^6$	$1{\cdot}5\times10^6$	1·12	0·075	$2{\cdot}0\times10^6$	1·49	Plat. to carb.
2	$2{\cdot}05\times10^6$	$2{\cdot}6\times10^6$	1·04	0·04	$3{\cdot}6\times10^6$	1·44	,, ,,

Omitting No. 5 of Series C, the following mean values may be assigned :—

Series.	$\left(\frac{1}{R}\frac{dR}{dv}\right)_0$.	v_m.	R_m/R_0.	Direction of current for $\left(\frac{dR}{dv}\right)_0$ positive.
C	0·67	0·285	1·10	Carb. to plat.
C′	1·46	0·057	1·08	Plat. to carb.

It will be seen that four of the contacts were of low resistance (under a thousand ohms), and the remaining three of high resistance. In the former the resistance *rises* for currents increasing from zero in the direction carborundum to platinum across the contact, whilst in the latter the resistance *falls* for currents in that same direction. Tests of the thermo-E.M.F.s obtained on heating the contacts showed that the thermo-electric power of the high resistance contacts was opposite in sign to that of the low resistance contacts. Apart from this striking evidence of heterogeneity of structure, the contacts of carborundum exhibit the same characteristic behaviour as galena and zincite, and thus fall within the same category of phenomena.

Other Minerals.—Experiments on the combinations of platinum-chalcopyrite and chalcopyrite-bornite show that the sensitiveness of these contacts is negligibly small compared with that of the preceding combinations. In the case of chalcopyrite-bornite three contacts were tested, the values of R_0 being respectively 1,952, 1,880 and 1,500 ohms. The corresponding voltage-coefficients at $v=0$ were 0·073, 0·05 and 0·00. Three contacts of platinum-chalcopyrite had resistances 160, 473 and 793 ohms respectively at $v=0$; the corresponding voltage-coefficients being 0·00, 0·00 and 0·026. A few contacts of platinum-zincite were also tested; they yielded values of $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$, R_m/R_0, and v_m, practically agreeing with those of chalcopyrite-zincite.

We may conclude that chalcopyrite, bornite and platinum are almost interchangeable elements of a combination whose other member belongs to minerals of the class zincite or carborundum. Bornite has the advantage of possessing a lower specific resistance than chalcopyrite.

The Thermo-electric Sign.—This was determined for all the above minerals in the manner indicated at the end of Section I. One element was platinum in each case.

TABLE V.—*Thermo-electric Sign of Minerals against Platinum.*

Material.	Direction of current across heated junction.
Zincite	Zincite to *Pt.*
Chalcopyrite	Chalcopyrite to *Pt.*
Bornite	*Pt* to bornite.
Galena	Galena to *Pt.*
Carborundum (low resistance)	Carborundum to *Pt.*
Carborundum (high resistance)	*Pt* to carborundum.

The characteristics shown in the Paper are drawn in accordance with the above results, the applied voltage being treated as positive when producing current across a junction in the same direction as that caused by a slight rise of temperature at that junction.

III. *The Thermo-electric Theory of the Phenomena.*

The contacts under investigation are such that on the one side the current passes across an area which may be of the order of a square centimetre, whilst on the other side it crosses an area many thousands of times smaller. Regarding the combination as a thermo-electric element, there will be a disengagement of heat on two accounts: Joulean heat, proportional to the square of the current and irreversible in sign; and Peltier heat, proportional to the current, and, therefore, reversed in sign when the current is reversed. The changes of temperature will be negligibly small at the junction of large area in comparison with that at the minute contact. We may, therefore, confine our attention to the latter only.

When the applied voltage is large—say, half a volt or higher—the heat at the contact is sufficiently great to cause appreciable softening, with consequent increase of contact area and drop of resistance. This effect supervenes earlier for current in one direction across the contact than when reversed.

The effects are simple provided the applied voltage is restricted to a sufficiently small value. In the account that follows this limitation is assumed.

Consider in the first place the case of a contact having zero temperature coefficient of resistance. If the Joulean heat could be neglected a rise of temperature would occur on applying a voltage in one direction, and an equal fall with voltage reversed. Equal and opposite thermo-E.M.F.s will be generated, the direction being such as in each case to *oppose* the applied voltage. The apparent resistance of the contact will be greater than the true resistance, the excess being independent of the direction of the current. Its value will be constant, since for small voltages the back thermo-E.M.F. will be proportional to the applied voltage. Now let us correct this result by taking the Joulean heat into account. For one direction of current this will be added to the Peltier heat, thereby increasing the rise of temperature and the back E.M.F., and consequently the apparent resistance. For current in the opposite direction the Joulean heat will partially neutralise the Peltier cooling; and the fall of temperature, the back thermo-E.M.F. and the apparent resistance will all be reduced. The resultant effect will be to give a straight line law connecting apparent resistance and applied voltage, the line being now inclined to the axis of voltage.

Another elementary thermodynamic principle of importance here is that when current across the junction causes Peltier *absorption* of heat, an external supply of heat must cause an E.M.F., and, therefore, a current, in the *same* direction across that junction. It follows that at a junction of materials possessing zero temperature-coefficients of resistance the apparent resistance *falls* when the current is of the same sign as that caused by heating the junction. Such a case is found in the combination manganin-constantan, observations on which are described below.

Let us next proceed to the case in which the specific resistances of the elements forming the contact vary appreciably with temperature. If the temperature coefficient is positive the effect will be to augment both the fall of resistance for one direction of current, and the rise for current in the reverse direction. The slope of the resistance characteristic in the immediate neighbourhood of zero voltage will be of the same sign as before, but increased in value.

When the temperature coefficient is negative, on the other hand, the slope of the characteristic at zero voltage is reduced, and changes sign when the coefficient is sufficiently large numerically, in which case we have a *rise* of apparent resistance when the current is in the same direction as that caused by applying heat to the junction. It will be shown that the large negative coefficients occurring in minerals like zincite and galena are amply sufficient to produce this rise. Thus is explained the apparent anomaly of a reduction in resistance despite the fact of a back thermo-E.M.F., and, vice versa, of a rise in resistance although the thermo-E.M.F. is in the direction to assist the applied E.M.F.

Attention may be further directed to the importance of the part played by a large negative temperature coefficient of resistance. Neglect of this consideration has given rise to fantastic views of the rises of temperature which must be invoked to account for actual resistance variations. Take, for example, the case of a zincite-chalcopyrite contact, at which was observed a fall of resistance from 20,000 ohms at zero voltage to 500 ohms under 1 volt. If temperature variation of resistance is neglected we are faced with the necessity of supposing a thermo-E.M.F. e in the direction of the applied voltage, such that $(1+e)$ volts across 20,000 ohms would produce the same current as 1 volt across 500 ohms—that is, e must be 39 volts. Assuming the thermo-electric power to be 1,000 microvolts per degree Centigrade, and independent of temperature, the required rise of temperature is 39,000°C. But if we suppose, on the other hand, zero thermo-electric power and a temperature variation of resistance at the rate of $-1{\cdot}5$ per cent. per 1°C., then assuming a compound interest law we have $20{,}000\ (1-0{\cdot}015)^t=500$, whence the rise of temperature is 243°C.; and we are back in the region of probability as well as possibility.

In working out an exact treatment of the actions which are assumed to take place at a contact the author is indebted to the Papers of Dr. W. Eccles * on this subject. Nevertheless the conclusions of the present Paper will be found to differ from those of the Paper quoted in several material respects.

Thus, whereas much importance is attached in the latter to the part played by the Thomson effect, in the present treatment the experimental results find their explanation in terms of the Peltier effect and the temperature coefficient resistance.

Again, the softening effect already referred to produces a considerable variation of resistance at the higher voltages, and this fact limits the range of voltage within which calculations can be made. This limitation renders unnecessary the supposition of a " dead resistance "; the elimination of the coefficient representing this allows of still further simplification and increased definitions in the final expressions obtained.

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* Eccles, " Proc." Phys. Soc., Lond., XXV., p. 273, 1913.

Let—

T=Absolute temperature at the contact.
T_0=Absolute temperature of the surroundings.
$t=T-T_0$=rise of temperature.
a=Thermo-electric power.
e=Thermo-E.M.F.
P=Peltier effect$=aT$.
i=Current.
v=Voltage.
$R=v/i$=apparent resistance.
R'=True resistance.
b=Temperature coefficient of true resistance.
H=Total rate of heat developed at contact.
K=Cooling coefficient.

Both v and i will be considered to be positive when in the direction of the current due to a slight heating of the contact.

Assuming the thermo-E.M.F. to be a linear function of temperature change,

$$e=at. \qquad (1)$$

Taking the rate of removal of heat from the contact to be proportional to temperature rise, then in the steady state,

$$H=Kt. \qquad (2)$$

R and R' are related as follows :—

$$\frac{v}{R}=\frac{v+e}{R'}. \qquad (3)$$

Assuming a linear variation of R' with temperature—

$$R'=R_0'(1+bt). \qquad (4)$$

The total heat developed at the contact by a current i is the sum of the Joule and Peltier effects. Observing the convention above defined for the positive direction of current, we have

$$H=i^2R'-Pi. \qquad (5)$$

On eliminating t, T, e, i, H, and P by aid of these relations we obtain the following expression for the apparent resistance of the contact in terms of the applied voltage :—

$$KR^2-R(KR_0'+a^2T_0)=v^2bR_0'-av(R+bT_0R_0'). \qquad (6)$$

This is the equation of the resistance-characteristic. Three main types of characteristic are derivable, which are represented diagrammatically in Fig. 5.

Type I. is the limiting case where $b=0$, when equation (7) simplifies to a straight line, denoting a resistance which falls for voltage applied in the positive direction. It is practically realised in the contact constantan-manganin.

Type II. includes all cases where b is positive, and thus covers all combinations of pure metals. With voltage in the positive direction the resistance at first falls, reaches a minimum, and afterwards rises.

Type III. represents cases for which b is negative and large. It includes all the mineral contacts possessing marked rectifying properties. The resistance *rises* at first with a positive voltage, reaches a maximum, and then falls continuously.

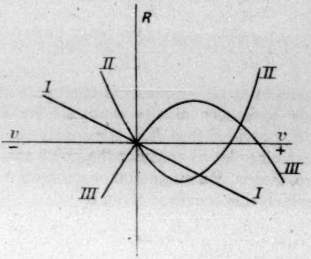

FIG. 5.—THREE THEORETICAL TYPES OF RESISTANCE CHARACTERISTIC.
Type I, $b=0$. Type II, b positive. Type III, b negative and large.

We now proceed to an examination of the values of $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$, R_m/R_0, and v_m which, it has been concluded from experimental observation, are constant quantities for any contact between the same pair of materials. It will now be shown that this constancy results from the theory, *provided* that the product KR_0 is a constant for the given pair of materials.

Putting $v=0$, equation (6), reduces to

$$R_0=R_0'+\frac{a^2T_0}{K}=R_0'\left(1+\frac{a^2T_0}{KR_0}\right). \quad . \quad . \quad . \quad . \quad (7)$$

The apparent resistance is greater than the true resistance by an amount proportional to the square of the thermo-electric power. Calculation shows that in the case of metals the term $\frac{a^2T_0}{KR_0'}$ is negligible compared with unity, and it is probable that in the case of minerals also its value is less than unity. Approximate results may, therefore, be obtained by neglecting the term in a^2 in equation (6).

Differentiating (6), we have

$$\frac{dR}{dv}=\frac{2bR_0'v-a(R+bT_0R_0')}{2KR-KR_0'-a^2T_0+av}. \quad . \quad . \quad . \quad (8)$$

There are two important special cases. First, let $v=0$. Then

$$\left(\frac{dR}{dv}\right)_0=\frac{-a(R_0+bT_0R_0')}{KR_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or

$$\left(\frac{1}{R}\frac{dR}{dv}\right)_0=\frac{-a(1+bT_0R_0'/R_0)}{KR_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The expression in (10) represents the value of the voltage-coefficient of resistance of the contact. Its value is independent of R_0 provided that KR_0 is a constant.

In the next place let us consider the point at which dR/dv is equal to zero, that is, R a maximum or minimum. The applied voltage at which this occurs is given by

$$v_m=\frac{a(R_m+bT_0R_0')}{2bR_0'}=\frac{a(R_m/R_0'+bT_0)}{2b}. \quad . \quad . \quad . \quad . \quad (11)$$

Substituting this expression for v in the general equation, we obtain a function of the form $f(R_m/R_0, KR_0)=0$, which means that provided KR_0 is independent of R_0, so also is R_m/R_0.

Returning to equation (11), and putting R_m/R_0' equal to a constant, we see that v_m necessarily becomes independent of R_0.

It follows, therefore, that on the thermo-electric theory of the effect the three quantities $\left(\frac{1}{R}\frac{dR}{dv}\right)_0$, v_m, and R_m/R_0 are independent of R_0, provided KR_0 is independent of R_0.

The Value of KR_0.—In seeking for a theoretical basis yielding the requirement that KR_0 should be a constant, or approximately a constant, for any given pair of materials, two views of the nature of the contact have been taken. From either of these the required condition can be deduced.

(*a*) We may assume ~~that the~~ contact resistance is given by the end-correction formula applied to, say, a uniform column of mercury in a capillary tube terminating within a considerable bulk of mercury. Applying Lord Rayleigh's formula to a contact supposed circular, of radius r, and denoting the specific resistance of the badly conducting component of the contact by ρ, we have

$$R_0'=\frac{0\cdot 8r}{\pi r^2}\rho=\frac{0\cdot 252\rho}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In the next place let us assume the heat to be developed symmetrically within a spherical volume whose linear dimensions are of the order of r of (12), and that the amount set free per unit volume at a point distant r from the centre of the sphere is proportional to r^n, where n is some constant. Then total heat developed per second within the sphere of radius r_0

$$=H=a\int_0^{r_0}4\pi r^2 \, . \, r^n dr=\frac{4\pi a r_0^{\,n+3}}{n+3} \quad . \quad . \quad . \quad . \quad (13)$$

where a is a constant.

In the steady state the heat crossing any isothermal surface is equal to the heat liberated within it. Denoting the thermal conductivity by k,

$$-4\pi r^2 k\frac{dt}{dr}=\frac{4\pi a r^{n+3}}{n+3},$$

whence

$$\frac{dt}{dr}=\frac{-ar^{n+1}}{k(n+3)}.$$

Hence for the excess of temperature t' of the centre over the boundary of the sphere we have

$$t'=\frac{a}{k(n+3)}\int_0^{r_0}r^{n+1}dr=\frac{ar_0^{\,n+2}}{k(n+2)(n+3)}. \quad . \quad . \quad (14)$$

Similarly the excess temperature t'' of the boundary of the sphere of radius r_0 over that of the surroundings is found to be given by

$$t''=\frac{ar_0^{\,n+2}}{k(n+3)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Adding t' and t'' the excess temperature t_0 of the centre of the sphere over that of the surroundings has the value

$$t_0=\frac{ar_0^{\,n+2}}{k(n+2)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Since $H=Kt_0$, we find from (13) and (16)

$$K=H/t_0=4\pi k r_0(n+2)/(n+3) \quad . \quad . \quad . \quad . \quad (17)$$

Now, according to (18) $K \propto r_0$; whilst by (12) $R_0' \propto \frac{1}{r_0}$. Combining (12) and (17),

$$KR_0' = 0{\cdot}8k\rho(n+2)/(n+3) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The value of this expression depends upon the ratio of the thermal and electrical conductivities, and is independent of the dimensions of the contact.

This same conclusion may also be reached if we assume

(*b*) That the resistance R_0 is located mainly—let us suppose entirely—in a thin film of molecular dimensions whose area is that over which the two elements of the contact intimately meet. There is an *a priori* improbability that the resistance of a mere contact such as is here under consideration can be calculated exactly as though the materials were welded in perfect molecular union across the minute area of the contact—which is really what is assumed in the view (*a*). According to the second view, to the resistance calculated on the lines of (*a*) should be added a resistance inversely proportional to the area of contact.

Assuming this latter contribution to be the main part of the total resistance, it follows that the Joulean heat, as well as the Peltier heat, is located in a thin film of molecular dimensions at the interface of the two materials. The stream lines of heat and of electricity will be similar in form. We shall have K proportional to the area of contact, and R_0 inversely proportional to the area of contact. KR_0 will thus be independent of the contact area, and proportional to the ratio of the thermal and electrical conductivities.

The Slope of the Resistance-Characteristic when $v=0$.—Equations (9) and (10) indicate how the gradient at zero voltage depends on the value of the temperature coefficient of resistance.

When b is positive, $(dR/dv)_0$ must be negative. The resistance assumes a minimum at the positive voltage v_m. This case, as well as the limiting case when $b=0$, is the subject of the experiments described in section IV.

When b is negative, the gradient becomes positive if $(1+bT_0R_0'/R_0)$ is negative, or since R_0'/R_0 differs little from unity, when $-b > \frac{1}{T_0}$. Now, in the case of minerals b is negative and often much larger numerically than for a pure metal. Thus, Pierce, in a careful determination, obtained the value

$-0{\cdot}0153$ for molybdenite at 0°C. There is thus an ample margin for concluding from thermo-electric theory that $(dR/dv)_0$ should be positive at mineral contacts, so that theory and observation are in agreement as to the direction of the rectified current under an alternating voltage.

IV. *Experiments with Metallic Contacts.*

Experiments on metallic combinations are of interest, since they supply the case where b is positive or zero. Moreover, the values of a and b are definitely known. The following were selected as test cases :—

Bismuth-Antimony.—a large, $b+$.
Iron-Nickel.—a fairly large, $b+$.
Constantan-Manganin.—a fairly large, $b=0$.
Copper-Manganin.—a very small, $b\doteq 0$.
Bismuth-Bismuth.—a zero, $b+$.

Attention was specially directed to the junctions bismuth-antimony and constantan-manganin. A series of contacts was examined in each of these cases, the results being to show (1) that the voltage-coefficient at zero voltage is independent of the resistance ; (2) that the sign of the above coefficient is negative ; (3) that a minimum occurs on the side of positive voltage.

We may conclude that the phenomena occurring at metallic contacts are thermo-electric in nature, and are essentially identical with those of mineral contacts.

The voltage coefficient is largest in the case antimony-bismuth, though even here it has only one-fifth the value found at a galena-platinum contact, and about one twenty-fifth that of a zincite contact. The specific characteristics of the above two contacts are shown in Fig. 10, which is drawn to the same scale as Fig. 2.

Softening of the Contact due to Rise of Temperature.—All the resistance-characteristics of this class exhibit a droop on both the positive and the negative side when the voltage rises to a certain value dependent on the duration of the current. It occurs most readily in contacts containing bismuth as one element, the melting point of which is 269°C. The effect is evidently due to softening and plastic yielding at the contact, which results in rapid increase of area. There is little doubt that this effect is present to an important extent in the case of mineral contacts also, though not so obvious since it then occurs on a falling characteristic.

Bismuth-Antimony.—An example of a characteristic is shown in Fig. 6. In order to obviate or diminish the softening effect the voltage was applied for only 0·003 second. The droop then occurs when v is between 0·3 and 0·4 volt. Four contacts were examined. The results of Table VI. show the constancy of the voltage-coefficient.

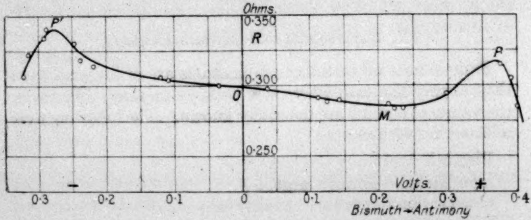

FIG. 6.—AN ANTIMONY-BISMUTH RESISTANCE CHARACTERISTIC.

TABLE VI.—*Bismuth-Antimony Contacts.*

No.	1.	2.	3.	4.	—
R	0·092	0·50	10·5	145·4	
(dR/d_0)	−0·019	−0·13	−2·75	−42·5	
$\left(\frac{1}{R}\frac{dR}{dv}\right)_0$	−0·206	−0·256	−0·26	−0·29	Mean = −0·254

At the lower range of voltage the characteristic is evidently of the type II. of Fig. 5.

Iron-Nickel.—The characteristic is of the same type as the last. The voltage-coefficient found was −0·16, and a minimum of resistance occurred at $v_m = 0{\cdot}016$ volt. The droops occur later than in the preceding case, and no difficulty was found in obtaining the point of minimum.

Constantan-Manganin.—This constitutes the case $b=0$. The characteristic equation (7) reduces to $R = R_0' - \frac{a}{K} \cdot v$, which represents a straight line. This linear type of characteristic was found as expected. An example is shown in Fig. 10; the duration of the applied voltage was 0·1 second.

The values of the voltage-coefficient for five different contacts are as follows :—

TABLE VII.—*Constantan-Manganin Contacts.*

No.	1.	2.	3.	4.	5.	—
R_0	0·0735	0·108	0·112	0·171	1·30	
$(dR/dv)_0$	−0·0083	−0·0095	−0·012	−0·0195	−0·133	
$\left(\frac{1}{R}\frac{dR}{dv}\right)$	−0·113	−0·088	−0·107	−0·114	−0·103	Mean = −0·105

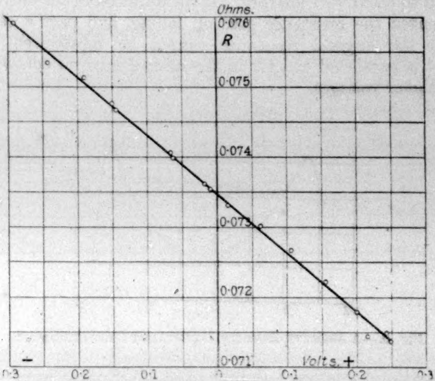

FIG. 7.—A CONSTANTAN-MANGANIN RESISTANCE CHARACTERISTIC.

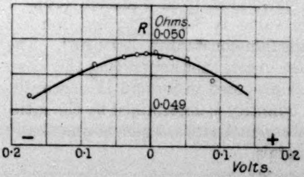

FIG. 8.—A COPPER-MANGANIN RESISTANCE CHARACTERISTIC.

Copper-Manganin.—Here $a \doteq 0$, $b \doteq 0$, so that on the theory R should be independent of v. Fig. 8 represents a specimen set of observations. The curve is symmetrical about the vertical axis. The slight fall is attributed to the softening effect.

A similar curve, though still flatter, was found with carbon-manganin.

Bismuth-Bismuth.—The object of this test was to examine the view of a softening due to rise of temperature. The characteristic, shown in Fig. 9, possesses a slight asymmetry due possibly to a slight difference in chemical quality of the two components of the contact. The anticipated droops were found to occur very sharply. If the duration of the current is prolonged the resistance goes on falling, and past a certain point the original resistance cannot be reproduced. The effect is paralleled exactly in the case of mineral contacts at the higher voltages.

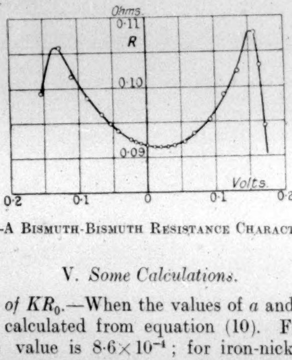

Fig. 9.—A Bismuth-Bismuth Resistance Characteristic.

V. *Some Calculations.*

The Value of KR_0.—When the values of a and b are known this can be calculated from equation (10). For antimony-bismuth the value is $8{\cdot}6\times10^{-4}$; for iron-nickel $4{\cdot}3\times10^{-4}$; and for manganin-constantan $3{\cdot}9\times10^{-4}$. These values are all of the same order, thus supporting the views of the nature of the contact proposed in Section IV., according to which the value of this quantity is determined by the ratio of the thermal and electrical conductivities, which is practically a constant in the case of metals.

The Ratio R/R'.—By equation (7) the ratio of the apparent and real resistance of a contact at zero voltage is given by the expression $(1+a^2T_0/KR_0')$. Applying the calculation to the case manganin-constantan, we have $a=40\times10^{-6}$, $KR_0=3{\cdot}9\times10^{-4}$, whence $a^2T_0/KR_0'\doteqdot0{\cdot}0012$, which is very small compared with unity. The same holds practically in the case bismuth-antimony.

The Rise of Temperature at the Contact.—Substituting for R the value $R_0'v(1+bt)/(v+at)$ derived from equations (1), (3) and (4), we obtain an expression for t in terms of v, which for small values of v reduces to

$$t=-v\,.\,\frac{aT_0}{KR_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The temperature change is thus proportional to the applied voltage and to the thermo-electric power. In the case of constantan-manganin the equation becomes $t=-30{\cdot}5v$, which denotes a fall of temperature for current in the direction constantan to manganin across the contact, at the rate of 30·5°C. per volt. For antimony-bismuth $t=-36v$. We may obtain an estimate in the case of mineral contacts by assuming values for (a) and (b). Thus, in the case of galena we may accept roughly $a=500\times10^{-6}$, $b=-0{\cdot}01$, whence $t=-177v$, *i.e.*, a fall at the rate of 177°C. per volt for current crossing the contact from galena to platinum.

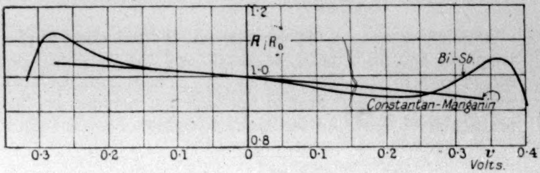

FIG. 10.—THE SPECIFIC RESISTANCE-CHARACTERISTICS OF TWO METALLIC CONTACTS.

The Value of v_m.—The agreement between the observed values of v_m and those calculated by equation (11) are shown in the Table below :—

Contact.	$a\times10^6$	b	R_m/R	v_m	
				Calculated.	Observed.
Iron-nickel	32	+0·004	0·998	0·008	0·016
Antimony-bismuth	100	+0·004	0·96	0·027	0·22
Galena-platinum ...	500 (assumed)	−0·01 (assumed)	1·04	0·05	0·066
Zincite-platinum ...	1,000 (assumed)	−0·01 (assumed)	1·54	0·136	0·15

VI. *The Reception of Electric Waves by the Contact Rectifying Detector. Conditions of Highest Sensibility.*

The law of constancy of the voltage coefficient can be applied to the receiving circuit in which a contact detector is employed in series with a magnetic telephone. It will be supposed, in the first place, that no polarising voltage is used. Since the oscillatory E.M.F. required to produce a signal is only a small fraction of a volt, the relation between R and v is practically a linear one. Let

$v=v_0 \sin pt$=applied voltage.
i=instantaneous current.
R=apparent resistance of contact.
R_t=resistance of telephone.
$A=\left(\frac{1}{R}\frac{dR}{dv}\right)_0$.

A simple treatment will be adopted, the induction of the telephone and leads being neglected and the resistance assumed to be independent of frequency. The conclusions thus reached may be corrected in the direction required by the practical conditions applying in any given case.

The current at any instant is given by

$$i=\frac{v_0 \sin pt}{R+R_t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Also

$$R=R_0(1+Av) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Hence

$$i=\frac{v_0 \sin pt}{R_t+R_0+R_0 A v_0 \sin pt}, \quad . \quad . \quad . \quad (22a)$$

which, since v_0 is considered small compared with unity, may be written with sufficient accuracy

$$i=\frac{v_0 \sin pt\left(1-\frac{AR_0}{R_t+R_0} \, . \, v_0 \sin pt\right)\sin pt}{R_t+R_0} \quad . \quad . \quad (22)$$

The mean or rectified current is

$$\frac{1}{T}\int idt=\frac{-AR_0 v_0^2}{2(R_t+R_0)^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Its value is proportional to the square of the R.M.S. value of the applied voltage, a result first empirically deduced by L. W. Austin.*

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* Austin, "Phys. Rev.," 1907.

The pull on the telephone diaphragm is determined by the number of ampere-turns. The best resistances of contact and telephone are those which make the ampere-turns a maximum for a given applied voltage. For maximum sensibility of receiving circuit, therefore, $\frac{nAR_0}{2(R_t+R_0)^2}$ must be a maximum, where n denotes turns on telephone.

Three cases will be discussed :—

i. The telephone supposed given, *i.e.*, n and R_t fixed. The ampere-turns are then proportional to $\frac{AR_0}{(R_t+R_0)^2}$, which is a maximum when $R_0=R_t$.

ii. The contact resistance supposed given. Assuming a constant weight of copper in the coil, and neglecting the correction for space occupied by insulation, we have $R=kn^2$. The required condition then reduces to $\frac{\sqrt{R_t}}{(R+R_0)^2}=$maximum. The solution is $R_t=\frac{1}{3}R_0$.

iii. The contact resistance and resistance of telephone variable at choice. The condition now is $\frac{R_0\sqrt{R_t}}{(R_t+R_0)^2}=$maximum. As R_0 is varied it is necessary, as the preceding case shows, to follow suit by rewinding the telephone so that $R_t=\frac{1}{3}R_0$. The condition thus reduces to $R_0^{-\frac{1}{2}}=$maximum. The smaller the resistance of contact and telephone the better. In practice, however, a limit to this reduction is evidently imposed by the impedance in other parts of the receiving circuit, which has not been considered.

To sum up, we conclude that for high sensibility :—

(1) The contact should be of materials having as large a voltage-coefficient as possible ;

(2) The resistance of the contact should be low (the lowest value depending on the impedance in receiving antenna, &c.) ;

(3) The resistance of the telephone should be about one-third that of the contact.

Use of a Polarising Voltage.—By applying the above considerations, and paying due regard to the form of the resistance characteristic for any combination, the effect of a polarising voltage may be foreseen. It is evident that if the polarising voltage be such as to lead to the point of maximum resistance on the characteristic, then the rectifying power and the sensibility become zero.

Again, if the resistance of the contact is below that of the telephone, it is quite possible that a polarising voltage in either direction may be deleterious or at least ineffective.

It is when the resistance of the contact happens to be much larger than that of the telephone that the advantage of a polarising voltage will be decisively seen. Its sign must evidently be chosen in the direction of the initial fall in the characteristic, *e.g.*, for the perikon the polarising current must cross the contact from chalcopyrites to zincite.

An examination of the curves shows that with voltages increasing from zero in the direction just specified, the slope of the characteristic at first increases. As the polarising voltage is increased further the slope at the corresponding points of the characteristic falls off, and evidently a value of the polarising voltage will be reached at which a maximum effect occurs. This value will depend on the initial resistance of the contact; it is thus not possible to specify any definite figure for the optimum polarising voltage at a contact of given materials.

Theoretically it appears that, given the receiving telephone, the ideal contact is one to which is applied the small polarising voltage leading to the point of maximum slope on the characteristic; and of initial resistance such that under that polarising voltage the resistance falls to a value exactly equal to that of the telephone.

VII. *Use of Direct-Current Galvanometer in Series with a Rectifying Contact in Null Alternating-Current Bridge Methods.*

This problem is amenable to the treatment applied in the last section. If the galvanometer be regarded as given, then for highest sensibility the resistance of the contact should be equal to that of the galvanometer, but if a given contact be taken then the best galvanometer to choose is one of resistance one-third that of the contact at zero voltage.

Treated as a millivoltmeter, we see that the arrangement shares with hot-wire instruments and dynamometers the defect that the square law is involved; and it may be shown that the minimum voltage detectable cannot be reduced greatly below a millivolt. For currents within the range of useful frequency of the telephone and the vibration galvanometer the combination of contact and direct-current galvanometer thus falls much below those instruments in sensibility. This conclusion is in accordance with experimental results.

The following example of a test may be quoted. The agreement between the observed rectified current and that calculated by equation (23) is very satisfactory :

Contact of galena-platinum : $A=1{\cdot}20$.
$R_0=95$ ohms.
Galvanometer resistance $=250$ ohms.
Sensibility $=186$ scale-divisions (1/40 in.) per microampere.
Applied voltage (R.M.S.) $=0{\cdot}05$ volt, at 85 $\sim$.
Observed steady deflection $=383$ scale-divisions ; whence rectified current $=2{\cdot}06\times 10^{-6}$ amperes.
Rectified current calculated by (23)

$$=\frac{1{\cdot}2\times 95\times 0{\cdot}05^2}{345^2}=2{\cdot}38\times 10^{-6} \text{ amperes.}$$

Taking half a scale-division as the minimum observable deflection, the minimum alternating voltage detectable with the given galvanometer and contact $=\dfrac{0{\cdot}05}{\sqrt{766}}=1{\cdot}81\times 10^{-3}$ volt.

Summary.

1. Measurements by the Wheatstone bridge have been made of the electric resistance at various rectifying mineral contacts ; the results being expressed in the form of resistance characteristics. The thermo-electric sign of the current was found in each case.

A series of similar measurements are recorded on contacts both elements of which are metallic.

2. A formula for the resistance characteristic is derived on the view that the phenomena in question are due to thermo-electric action. The experimental results are shown to be fully explained on this view. The fact that the rectified current (when an alternating voltage is applied) is generally, in the case of mineral detectors, in the opposite direction to that produced by heating the contact, is shown to be in harmony with the thermo-electric view, and not, as has generally been supposed, in collision with it. The determining factor in respect of sign proves to be a large negative temperature coefficient of resistance.

3. In relation to the thermo-electric theory, two views as to the location of the resistance at a contact are proposed and discussed.

4. Some calculations, including that of the rise of temperature at a contact, are given.

5. The experimental results form the basis of calculation of the best values to chose for the resistances of the contact and telephone in a wireless receiving circuit.

6. The influence of a polarising voltage on the sensibility of the receiving circuit is discussed.

7. It is shown that the combination of direct-current galvanometer and sensitive contact cannot respond to an alternating voltage much below 1 millivolt.

8. Observed values of rectified current are found to be in close agreement with those calculated on the thermo-electric theory.

ABSTRACT.

The Paper contains an account of an investigation, the primary object of which was to determine the nature of the physical actions occurring at a rectifying contact. Resistance characteristics are given for various contacts, some including a mineral, some in which both elements are metals. It is shown that a *specific characteristic* may be drawn for any given pair of materials. The experimental results are in accordance with the view that the actions are thermo-electric, the main determining factors being the thermo-electric power and the temperature-coefficient of electric resistance.

Based on the law of constancy of the voltage-coefficient calculations are given showing the best value of the resistance of the telephone in a wireless receiving circuit in which the contact detector is employed. The influence of a polarising voltage is also traced.

The use of the combination of rectifier with a direct-current galvanometer as indicator of the balance point in an alternating-current bridge is examined, and it is shown that the minimum detectable alternating voltage cannot be reduced much below a millivolt.

DISCUSSION.

Mr. Duddell thought the Paper was a very important contribution. He had no definite opinion as to the true explanation of rectifying contacts. In practice very much depends on the exact part of the crystal at which contact is made. With regard to thermo-electric forces, he had examined a large number of crystals in the hope of obtaining contacts which were more stable than those ordinarily employed, and he had concluded that no mineral which did not show thermo-electric effects was of any use as a detector. There might be exceptions in the case of metals, but the rule applied to all sulphides. His experience with regard to the receiving telephone differed somewhat from the author's. In a telephone the resistance and impedance depend on the frequency. In practice it seemed desirable to keep the impedance of the telephone of the same order as the resistance of the detector, and adjust the latter until the desired sensitivity is attained. In receiving strong signals one may employ very tight contacts in which it appears to be impossible that there should be any air film. A satisfactory rectifying action is still, however, obtained.

Prof. G. W. O. Howe thought that it was well to avoid flying off to new hypotheses in order to explain new phenomena if they could possibly be accounted for on well-known grounds. He was pleased to see that the author had been able to explain rectifying contacts without invoking any mysterious new properties. He was rather surprised to gather from the author's remarks that the thermo-electric theory was generally discredited. His impression had been that the work of Dr. Eccles had established it as the accepted explanation. Had any of the exponents of the electron theory attempted to give a detailed explanation of the observed phenomena on that basis? What was the origin of the "settling down" of contacts mentioned by the author? Was it a mechanical or thermal effect? He would like to hear just in what respect the results of Mr. Owen's work differed from those of Dr. Eccles.

Dr. W. Eccles remarked that he was glad to find such agreement on the absurdity of rushing to special explanations of these phenomena. Certain workers had thought that electrostatic attraction altered the area of contact. Others assumed the opening of trapdoors to let electrons through, the mechanism of the process being considerably more difficult to explain than the original results themselves. Prof. Fleming had found that many of the substances used as detectors were photoelectric—*i.e.*, they give off electrons under the action of light—and he assumed that rectifying phenomena were caused by a similar action of the longer electro-magnetic waves. He (Dr. Eccles) had tried to put these points straight by explaining the phenomena in terms of well-known physical properties, such as the resistance coefficient, Peltier effect, &c., and had found it possible to account for all the effects. The theory proved unpopular because it had nothing occult about it. Mr. Owen had dropped the Thomson effect from his treatment. He thought this was not justifiable, as the Thomson effect was a physical fact which must enter into the result in practice. Leaving it out of consideration simplifies the treatment, but loses the explanation of several of the erratic properties of detectors. For instance, the theoretical resistance characteristic curves obtained by Mr. Owen are parabolic. It is obvious, however, that the experimental curves are of the fourth degree. The Thomson effect must be introduced to explain the way the curve bends off at the extremities. One important result of the author's was that for the same materials the value of R_m/R_0 was constant for any contact, light or heavy. This appeared to him to be due to the fact that increasing the area of contact by increasing the pressure was equivalent to putting two or more similar contacts in parallel.

Mr. A. F. Hallimond (communicated): I should like to congratulate the author on his reduction of the curves for each contact-pair to a specific resistance characteristic. If it is found that the same process can be employed in all cases a very useful and simple means of comparison will be established. The result seems the more remarkable in being based upon the resistance-curves, and I should like to ask whether the relation throws any light on the conditions obtaining at the contact when the pressure is varied. With reference to the heating of the contact, I believe that Prof. Pierce observed that at 80 cycles no lag occurred, such as might be due to heating. The author's arrangement by which the current may pass from 0·003 second would seem to be even more sensitive. Was any variation observed in the resistance with the time of passage of the current? With regard to the thermal effects, might I suggest the investigation of pyrite, a mineral in which adjoining areas may exhibit widely different thermal E.M.F.s?

Mr. P. R. Coursey communicated the following remarks: The three main results arrived at will be of especial value, even if they do no more than form a basis of comparison for the work of different investigators, which up to the present has only been applicable (quantitatively) to the particular contacts on which the experiments were made. I should, therefore, like to ask the author whether he has found the "specific resistance characteristics" that he has obtained to be applicable to results derived from measurements on different crystals of the same materials, or merely to contacts of various pressures and resistances between individual crystals. The two very different curves given for carborundum crystals would seem rather to support the latter view. As to the accuracy of this method of determining the characteristic, it would not seem to possess much ultimate advantage where very small voltages are concerned, as in any case the limit of accuracy depends on the galvanometer employed, whether for the direct measurement of the current passing through the crystal or for the indication of balance of the bridge. Moreover, the method of obtaining the resistance with very brief currents, although leading to consistent results from the "curve" point of view, scarcely corresponds to the use in practice of a steady polarising or boosting voltage (often of the order of 1 volt, as is usual, for instance, with most carborundum crystals) which may be impressed on the crystal for many hours at a time, and would, therefore, probably produce a maximum of softening effects at the contact. It would, therefore, be interesting if a series of curves could be obtained with different contact times in order that the magnitude of this effect might be gauged. On the other hand, it is just possible that if any appreciable temperature rise occurs at the contact this factor of itself may cause an increase in the sensitiveness of the detector, quite apart from the purely electrical effect of the applied voltage. These considerations, however, perhaps affect rather the practical applications of the detectors than the physical processes underlying their action with which the Paper is chiefly concerned.

The **Author** (in reply) said he was glad to learn that it was Mr. Duddell's uniform experience that high thermo-electric power and sensitiveness of a contact detector go together. In regard to the relation of impedance of telephone to the resistance of the contact he was quite prepared to find that the conclusions deduced from the simple treatment employed in the Paper required modification to conform to the actual conditions of practice. In reply to Prof. Howe's inquiry as to the cause of the "settling down," this was not due to thermal action; the small testing voltage was applied only at intervals, and was not itself the cause of the change described. The effect appeared to be of the nature of an adjustment of the molecules bounding the contact when their setting was changed; it was probably allied to the slow changes met with in the study of elastic strains. He did not go so far as to say that the thermo-electric theory had become generally discredited, but rather that it stood in need of confirmation. He would endeavour briefly to point out in what relation his own work appeared to stand to that of Dr. Eccles; this reply would cover some points of difference which Dr. Eccles had commented upon. Dr. Eccles employed coefficients representing the Peltier effect, the Thomson effect, and the temperature coefficient of resistance. The author finds that the existence of softening and consequent increase of area of contact due to rise of temperature becomes very important at the higher voltages. This effect is complicated and thus not amenable to mathematical treatment; the course adopted in the present Paper is, therefore, to restrict the application of the formulæ within small limits of voltage—say, a few tenths of a volt. Apart from this, the chief point of difference is in the emphasis laid on the relative value of the coefficients. The author finds that the experimental results in the case of all the mineral and metallic contacts tested may be explained without invoking the Thomson effect; the conclusion is, therefore, drawn that this term is of small importance in comparison with the Peltier effect, at all events at low voltages. It thus fortunately becomes possible to simplify the theory appreciably. Again, in the author's view not only does resistance admit of more precise measurement, but the statement of results in the form of resistance characteristics brings out the essential features of the behaviour of these contacts more clearly than if current characteristics are employed. In reply to Mr. Hallimond, the determination of resistance of contact as a function of pressure is not specially considered in the Paper. The tests here recorded tend, however, to show that pressure only enters in so far as it alters the area of contact. In regard to the question of time-lag, this is the subject of experiments now in progress. In reference to pyrite, the author fully grants that heterogeneity may and does exist in this and other cases; for further instance, in the high and low-resistance specimens of carborundum referred to in the Paper, both possessing high thermo-electric power, but of opposite signs in the two cases.

In reply to Mr. Coursey's first question, it is a matter for experiment to discover to what extent various specimens of nominally the same mineral agree in behaviour. Reference may be made to the remarks immediately preceding. As to the matter of accuracy, the bridge method carries the advantage that a null method has over a deflectional one; and, further, that of permitting of practical elimination of the effects caused by prolongation of time of application of applied voltage. It is, of course, true that when a polarising voltage is applied the time effect must enter; but even here the all-important changes caused by the superposition of a rapidly oscillatory voltage are in themselves independent of softening action.

XIX.—*The Latent Heat of Fusion of a Metal and the Quantum-Theory.*

By H. STANLEY ALLEN, *M.A., D.Sc., University of London, King's College.*

§1. When a pure crystalline solid is heated, fusion takes place over the surface only at a definite temperature, T. The atomic heat of fusion of the solid is the number of calories required to melt 1 gram atom at this temperature, *i.e.*, it is AL, where A is the atomic weight and L is the latent heat per gram.

The energy supplied to melt the solid may be identified with the work that must be done to break the bonds which impart to the solid its crystalline structure. The molecules liberated by the breaking of the bonds are, in general, free to move amongst their neighbours, so giving the mobility of the liquid state.

According to the quantum-theory, the energy of a solid is the energy of the oscillators present. From this standpoint it would appear that the latent heat of fusion may be identified with the energy necessary to counterbalance that of a certain number of these oscillators. In this theory the average amount of energy that is associated, at absolute temperature T, with a vibration of frequency ν is supposed to be

$$RT \times \frac{x}{e^x - 1},$$

where x stands for $h\nu/RT$, h is Planck's constant and R is the gas constant for a single molecule. This expression is employed both by Einstein and by Debye in discussing the theory of the specific heat of a solid.*

Let c denote the ratio of the number of oscillators concerned in holding together the crystalline structure to the number of atoms, then the number of these oscillators in 1 gram molecule is Nc where N is Avogadro's constant. We now assume as the fundamental equation for the latent heat of fusion of a monatomic metal

$$AL = cNRT \times \frac{x}{e^x - 1}. \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

Hence

$$\frac{AL}{NRT} = c\frac{x}{e^x - 1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

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* Jeans, "Report on Radiation and the Quantum-Theory," Ch. VI., 1914.

Here NR is the value of the gas constant for 1 gram molecule, which is known to be 1·989 calories per gram molecule per degree.

To be able to test the validity of the hypothesis it is necessary to know the value to be assigned to ν, the frequency of the oscillator concerned in the change of state, at the temperature of the melting point. For this purpose the formula of Lindemann* has been employed. This gives

$$\nu=k\sqrt{\frac{T}{AV^{\frac{2}{3}}}}, \quad . \; . \; . \; . \; . \; . \; . \quad \text{(iii.)}$$

where V is the atomic volume and k is a multiplying factor, whose value, deduced empirically from the case of silver, is $2{\cdot}12\times10^{12}$. The formula was found by Lindemann to give results in fair agreement with those determined from the atomic heats by Einstein's formula in the case of the elements Pb, Cu, I, Pt and Si.

TABLE I.—*Experimental Constants for the Metals.*

Metal.	*A.*	*L.*	*T.*	*V.*	ν.
Aluminium	27·1	76·8	931	10·1	$5{\cdot}75\times10^{12}$
Bismuth..................	208·0	12·64	541	21·2	1·24
Cadmium	112·4	13·66	593·7	13·0	2·07
Cæsium	132·81	3·766	301·4	71·0	0·77
Copper	63·57	42·0	1,356	7·1	*4·93
Gallium	69·9	19·0	303	11·79	1·94
Iron	55·84	59·0	1,803	7·1	6·27
Lead	207·1	5·36	600	18·2	*1·44
Mercury	200·6	2·82	234	14·8	9·33
Nickel	58·68	4·64	1,708	6·7	6·07
Palladium	106·7	36·3	1,818	9·3	4·16
Platinum	195·2	27·2	2,028	9·1	*3·1
Potassium	39·1	14·67	336·5	45·5	1·74
Rubidium	85·45	6·144	312	56·0	1·06
Silver	107·88	21·07	1,234	10·3	*3·3
Sodium	23·0	27·21	370·9	23·7	2·96
Tin	119·0	14·0	505	16·2	1·73
Zinc	65·37	28·13	692	9·5	3·26

* Lindemann.

§2. The data available for the latent heats of the metals are limited, and there can be no doubt that the values in many cases are subject to a large percentage error. The values for L and T in Table I. are taken from the Smithsonian Physical Tables (1914) and "Recueil des Constantes Physiques" (1913), with the exception of those for the alkali metals, which have been investigated recently by Rengade.* The temperature of the melting point is given on the absolute scale. The values for the atomic volumes are those given by Richards.†

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* Lindemann, "Phys. Zeitschr.," Vol. XI., p. 609, 1910.

§3. In Table II. are given the values of the change in entropy, AL/T, and of AL/NRT, arranged in order of magnitude. The calculated values for the latter quantity were obtained by assigning to the factor c a value which was either unity or a simple fraction, as shown in the last column of the Table. It must be noticed that the value assigned to c is based on the assumption that the element is monatomic. If this be not the case, Lindemann's formula and the value of c may require modification.

Table II.—*Atomic Latent Heat of the Metals.*

Metal.	AL/T.	AL/NRT.		
		Obsd.	*Calcd.*	c.
Nickel	(0·159)	(0·080)	0·915	1
Caesium	1·66	0·835	0·939	1
Rubidium	1·68	0·845	0·919	1
Sodium	1·69	0·850	0·809	1
Potassium	1·70	0·855	0·878	1
Iron	1·827	0·919	0·918	1
Silver	1·842	0·926	0·915	1
Lead	1·850	0·930	0·942	1
Copper	1·969	0·990	0·915	1
Palladium	2·130	1·07	0·946	1
Aluminium	2·236	1·12	1·143	4/3
Mercury	2·418	1·22	1·208	4/3
Cadmium	2·586	1·30	1·221	4/3
Platinum	2·618	1·32	1·289	4/3
Zinc	2·657	1·34	1·338	3/2
Tin	3·299	1·66	1·609	7/4
Gallium	4·382	2·20	2·182	5/2
Bismuth	4·860	2·44	2·363	5/2

A comparison between the calculated and the observed values of AL/NRT shows moderately good agreement, perhaps as much as we have any right to expect in view of the uncertainty attaching to some of the quantities involved. In the case of the alkali metals it will be noticed that the order for the calculated values is that of the periodic table. The observed values for rubidium and cæsium are probably under-estimates. It is clear that the value recorded for the latent heat of nickel (4·64 calories per gram, Pionchon, 1887) is not appropriate for a pure crystalline solid of melting point 1,708°K. It is more likely to represent the value for a mixture of crystalline and amorphous material. The well-known modifications in the magnetic properties of nickel resulting from temperature changes are in agreement with such a view.

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* Rengade, "C.R.," Vol. CLVI., p, 1897, 1913.

† Richards, Am. Chem. Soc. "Journ.," Vol. XXXVII. p. 1643, 1915.

§ 4. Oxley* has pointed out that intense local molecular fields are necessary to account for the rigidity of a crystalline structure. If the field be interpreted as a magnetic field the strength must be of the order 10^7 gausses, and "the amount of potential energy associated with 1 gm. of the crystalline medium in virtue of its molecular grouping" must be about 10^9 ergs. "The thermal equivalent of this will be of the order $10^9/4 \cdot 10^7 = 25$ gm. calories, which represents the heat energy required to destroy the crystalline structure—*i.e.*, the latent heat of fusion."

Without discussing the particular interpretation of the molecular field put forward in Oxley's Papers, it will be seen that his view of the latent heat of fusion is not inconsistent with that here adopted.

In 1897 Prof. Richards† concluded that the atomic heat of fusion of a metal is usually $\frac{1}{3}$ (or $\frac{1}{2}$ or 1) the heat required to raise the temperature of the metal from absolute zero to the melting point T, or, assuming the law of Dulong and Petit, AL is approximately $2{\cdot}1\ T$. The figures recorded in Table II. do not lend much support to this view.

Attempts have been made to find expressions for the latent heat of fusion of compounds, and some of these are of interest in connection with the present discussion.

Crompton‡ in 1895 suggested that the latent heat of fusion could be calculated from the formula,

$$ML/T\Sigma v = \text{a constant } (1{\cdot}38),$$

where M is the molecular weight and Σv the sum of the valencies. There is a certain correspondence between this formula and equation (ii.) of the present Paper, for the latter may be re-written as

$$AL/Tc = NR\frac{x}{e^x - 1}.$$

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* Oxley, "Phil. Trans.," Roy. Soc. A, Vol. CCXV., p. 93, 1914.

† Richards, "Chem. News," Vol. LXXV., p. 278, 1897.

‡ Crompton, "Journ." Chem. Soc., Vol. LXVII., p. 315, 1895.

Since $\frac{x}{e^x-1}$ in the cases considered is not far from unity, the right-hand side of this equation is very approximately constant.

Walden,[*] from analogy with the Pictet-Trouton rule for the latent heat of vaporisation, gave the relationship ML/T $=$constant. According to Tamman,[†] the latter rule is of doubtful validity, as only about one-quarter of the substances examined gave values for the constant falling within the limits 15·8 to 12·0 suggested by Walden. "Metals give constants ranging from Bi 4·82 to K 1·84."

§ 5. *Application of Debye's Theory.*—The form of quantum-theory employed above is that due to Einstein, in which all the vibrations in a solid at a specified temperature are assumed to have the same frequency, ν. It is known that this theory is imperfect, and must be regarded as at best a first approximation to the truth. In the theory of Debye[‡] the frequencies are dependent on the elastic constants of the solid, and may assume all values between zero and a certain maximum value, ν_m. "His theory is based on a number of hypotheses which cannot be accepted as being strictly valid, but of the formulæ hitherto published for the representation of the atomic heat curves of the metals that of Debye gives the closest approximation to the experimental results."[§]

I have attempted to apply this theory to the determination of the latent heat of fusion by finding the energy in a substance at the melting point both in the state of solid and in the state of liquid. Unfortunately, the only metal for which the compressibility has been determined when liquid is mercury. In this case the theory does not give a result in harmony with experience. The result is improved somewhat by the introduction of a zero point energy, as in the later form of Planck's theory. If the energy of an oscillator be taken as

$$\frac{h\nu}{e^{h\nu/KT}-1}+ah\nu,$$

close agreement between the observed and the calculated values of the latent heat can be obtained by assuming $a=\frac{4}{3}$, instead of the usual assumption $a=\frac{1}{2}$. This assumption is, however, entirely arbitrary, and there is no theoretical ground for adopting it. Determinations of the compressibility of other metals in the liquid state are much to be desired.

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[*] Walden, "Zeitschr. Elektrochem.," Vol. XIV., p. 713, 1908.

[†] Tamman, "Gesell. Wiss. Göttingen," Vol. III., p. 335, 1913.

[‡] Debye, "Ann. de Physik," Vol. XXXIX., p. 789, 1912.

[§] E. H. Griffiths and E. Griffiths, "Proc." Roy. Soc., A, Vol. XC., p. 559, 1914.

§ 6. To sum up the results of the present Paper, it may be said that the atomic heat of fusion of a metal can be calculated with fair accuracy on the basis of the quantum-theory by assuming that the latent heat represents the energy of a certain number of oscillators having a frequency at the melting point which can be found from the formula of Lindemann.

ABSTRACT.

The latent heat of fusion is identified with the energy necessary to counterbalance that of a certain number of "oscillators" concerned in holding together the crystalline structure. Assuming that the energy of an oscillator having a vibration frequency ν is

$$RT\times\frac{x}{e^x-1},$$

where x stands for $h\nu/RT$, it is found that the atomic heat of fusion of a metal can be calculated with fair accuracy by the formula,

$$AL=cNRT\times\frac{x}{e^x-1}.$$

Here A denotes the atomic weight, L the latent heat, and c the ratio of the number of oscillators in question to the number of atoms. Thus, the number of oscillators in 1 gramme molecule is Nc, where N is Avogadro's constant. It is found that to the factor c must be assigned a value which is either unity or a simple fraction. The frequency at the temperature of the melting point is calculated by means of the formula of Lindemann. The application of Debye's theory is also discussed.

DISCUSSION.

Dr. R. S. **Willows** agreed with Dr. Allen that the quantum-theory was still in a very speculative state. He referred to the statement in § 1, that "*The energy supplied to melt the solid may be identified with the work that must be done to break the bonds which impart to the solid its crystalline structure.*" This seemed to rule out of consideration the case of amorphous solids. It is supposed that some of the alterations produced in a metal by treatment such as rolling are due to some of the molecules becoming amorphous. Could the theory be extended to deal with the change from the crystalline to amorphous states ?

Dr. **Allen** thought the change from crystalline to amorphous conditions was the same as from crystal to liquid.

Prof. **Boys** : Would not that imply that there was no latent heat in amorphous material ?

Dr. **Allen** agreed that that would be implied.

Mr. **Ezer Griffiths** communicated the following remarks : Could the author give a clearer conception of the theory advanced to explain the process of liquefaction on the quantum-theory, and in particular of the statement "that the latent heat of fusion may be identified with the energy necessary to counterbalance that of a certain number of these oscillators ?" Was this statement in harmony with that postulated by Lindemann in

obtaining the frequency ν—namely, "that the melting point is determined by the fact that at this temperature the amplitudes of the vibrations of the atoms around their position of rest become commensurable with the atomic distances—*i.e.*, it is the collision of the atoms which produce the destruction of the crystalline form?" Further, the statement that "the energy of a solid is the energy of the oscillators present" needed some qualification, particularly at high temperatures. Sodium, for example, had an atomic heat just below the melting point 7·5, while the calculated value was only about 6·5.

Communicated reply to Mr. Ezer Griffiths: I have refrained of set purpose from attempting to give an exact description of the process of fusion, or of the nature of an "oscillator." It is characteristic of the quantum-theory that it is capable of interpretation in various ways, and different mechanisms might, no doubt, be imagined which would satisfy the requirements of the theory.

Personally I regard Lindemann's formula as largely empirical, but I do not think the theory of my Paper is inconsistent with the view of Lindemann, if that be expressed by saying that the destruction of the crystalline form is conditioned by (not necessarily produced by) the collision of the atoms.

It is known that at high temperatures complications may arise—*e.g.*, through the rotations of the atoms or molecules (Jean's Report, pp. 76, 77), but I have not attempted to deal with these at the present stage of the work.

XX. *Lenses for Light Distribution.* *By* T. Smith, *B.A.* (*From the National Physical Laboratory.*)

Received April 1, 1916.

The conditions to be satisfied by the lenses of motor car headlights, ship's sidelights and headlights and a number of other lenses used to illuminate near or distant objects or to indicate the presence or position of a ship or other body are so dissimilar from those involved in what are ordinarily included among optical instruments that these lenses cannot be satisfactorily designed on the principles successfully employed in determining the forms for the lenses of the more usual class of optical instruments. A method which is applicable to the kinds of lenses enumerated above will be apparent from the discussion of a special case.

The starboard and port lights of steamers are required to be visible over a definite extended horizontal angle from as great a distance as possible. Owing to the rolling of the ship it will not be satisfactory to project the light with a very small vertical divergence from the horizontal plane. On the other hand, the visibility required is such that with the available sources of light and the desired size of lantern the necessary horizontal intensity cannot be secured over the whole vertical angle which it is desired to illuminate.

In connection with an investigation by Paterson and Dudding on the visibility of ships' navigation lights it was desired to obtain uniform intensity in the projected beam over the angle between 5 deg. of elevation and 5 deg. of depression, and to let the intensity fall off uniformly outside these limits at such a rate that when the lantern was inclined at 15 deg. to the horizontal the visibility at a considerable distance would be equal to that of the central beam at twice that distance.

Fig. 1 gives the relation between the intensity and the angle of elevation or depression when half visibility is required at 15 deg.

The same light distribution is required for all azimuths, and the lenses are, therefore, cylindrical with the source of light on the axis of the cylinder. If this source may, with sufficient accuracy, be considered a line source coincident with the axis of the cylinder the problem becomes two dimensional.

It has been customary in the past to make the inner surfaces of these lenses in the form of a right circular cylinder, and this form is adopted in the present case. The general dimensions of the lamps now in use, in which the distance of the inner glass surface from the vertical axis is from 4 in. to $4\frac{1}{2}$ in. and the vertical aperture of the lenses from 6 in. to 7 in. are also adhered to. These dimensions have a very appreciable influence on the shape of the lens, since the ratios of these lengths to the height of the source of light are some of the most important among the factors which determine that shape. When electric glow lamps are used this height may be easily adjusted to suit the dimensions of the lantern, but as it is necessary for the same lanterns to be suitable for use with lamps burning colza or paraffin, the height of the source of light to be used is fixed within comparatively narrow limits.

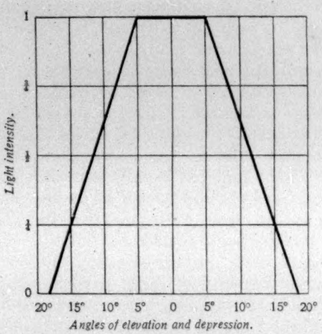

Fig. 1.

There are two distinct cases that may arise : in the one the decline in the light intensity beyond 5 deg. is due to the eclipse of part of the light source by the lens mount, total eclipse taking place at the extreme angle at which any light is emitted ; in the other, the falling off is due to a change in the curvature of the outer lens surface. In general, the former type requires a high light source, the latter a comparatively short one. In both types the internal principal focus of the lens must be further from the lens than the axis. The mathematical treatment of the former case is not simple, and will not be given here, as the conditions rarely apply to practical cases.

Suppose, then, that a small linear source of light is coincident with the axis of the system which is assumed to be symmetrical with respect to the horizontal plane bisecting the source.

Let a ray of light start from the source making an angle θ with the horizontal until it meets the inner glass surface of radius a. After refraction let it make an angle φ with the horizontal, and be refracted from the lens at an angle β, the tangent to the refracting surface making an angle α with the vertical. Then, if μ is the refractive index of the glass

$$\sin \theta = \mu \sin \varphi,$$

and
$$\mu \sin (\alpha - \varphi) = \sin (\alpha - \beta).$$

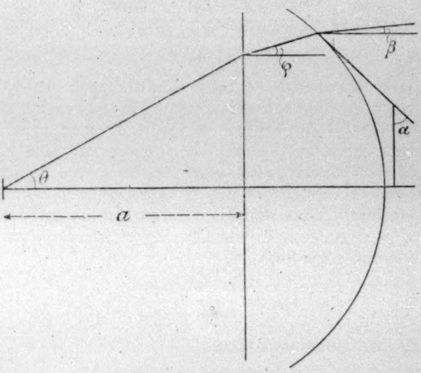

FIG. 2.

Denote by β_1 the angle (in this case 5 deg.) up to which the visibility is to be the same as that on the axis, and by β_2 the extreme angle at which light, in the ideal case, will emerge from the lens. Let θ_1, φ_1 and θ_2, φ_2 be the corresponding values of θ and φ. Then only that light is useful which is emitted from the source between angles $-\theta_2$ and $+\theta_2$ with the horizontal. The intensity of the light emitted at the angle θ is proportional to $\cos \theta$, and, therefore (considering, say, the upper half of the lens) the light emitted between the angles o and θ bears to that emitted between o and θ_2 the ratio $\sin \theta / \sin \theta_2$. Now from Fig. 1 the ratio of the total amount of light emerging between angles o and β to that between angles

o and β_2 is to be $2\beta/(\beta_1+\beta_2)$, if $\beta<\beta_1$, and $1-\dfrac{(\beta_2-\beta)^2}{\beta_2^2-\beta_1^2}$ if $\beta>\beta_1$. The rays incident upon the first lens surface which divide the total energy in a given ratio must correspond with the emergent rays which have the same value for this ratio, neglecting all losses due to reflection and absorption. Thus, the conditions

$$\frac{\sin\varphi}{\sin\varphi_2}=\frac{\sin\theta}{\sin\theta_2}=\frac{2\beta}{\beta_1+\beta_2},\ \text{or}\ \frac{\sin\varphi}{\sin\varphi_1}=\frac{\sin\theta}{\sin\theta_1}=\frac{\beta}{\beta_1},\ \text{if}\ \beta<\beta_1,$$

and

$$\frac{\sin\varphi}{\sin\varphi_2}=\frac{\sin\theta}{\sin\theta_2}=1-\frac{(\beta_2-\beta)^2}{\beta_2^2-\beta_1^2},\ \text{or}\ \frac{\sin\varphi}{\sin\varphi_1}=\frac{\sin\theta}{\sin\theta_1}=\frac{\beta}{\beta_1}-\frac{(\beta-\beta_1)^2}{2\beta_1(\beta_2-\beta_1)}$$

if $\beta>\beta_1$

secure the distribution of light shown diagrammatically in Fig. 1 when the light source is small. The application of these formulæ enables the outline of the lens to be constructed geometrically in any given case. Applying them to the assumed conditions, with glass of refractive index 1·5, $a=100$ mm., aperture$=160$ mm., it is found that $\theta_2=38{\cdot}7$ deg., $\sin\theta_2=0{\cdot}6252$. Thus, dividing the light in the half lens into 12 equal parts, and sub-dividing the last section into four equal parts, and using the formula,

$$\tan a=\frac{\mu\sin\varphi-\sin\beta}{\mu\cos\varphi-\cos\beta},$$

the following figures are obtained :—

β	Sin θ.	Sin φ.	θ	φ	μ Cos φ.	Tan a.	a.
Deg.			Deg.	Deg.			Deg.
0·000	0·0000	0·0000	0·000	0·000	1·5000	0·0000	0·000
0·972	0·0521	0·0347	2·987	1·988	1·4991	0·0699	4·000
1·944	0·1042	0·0695	5·981	3·983	1·4964	0·1412	8·039
2·917	0·1563	0·1042	8·992	5·981	1·4922	0·2140	12·078
3·889	0·2084	0·1389	12·028	7·983	1·4855	0·2882	16·078
4·861	0·2605	0·1737	15·099	10·005	1·4772	0·3656	20·084
5·861	0·3126	0·2084	18·215	12·028	1·4670	0·4454	24·010
6·947	0·3647	0·2431	21·388	14·071	1·4550	0·5271	27·795
8·149	0·4168	0·2779	24·631	16·135	1·4409	0·6098	31·375
9·514	0·4689	0·3126	27·960	18·215	1·4249	0·6920	34·684
11·132	0·5210	0·3473	31·397	20·324	1·4067	0·7706	37·618
13·241	0·5731	0·3821	34·964	22·463	1·3865	0·8350	39·862
13·924	0·5861	0·3907	35·880	23·000	1·3807	0·8425	40·113
14·733	0·5991	0·3994	36·807	23·544	1·3752	0·8449	40·193
15·787	0·6121	0·4081	37·745	24·088	1·3693	0·8364	39·910
18·333	0·6252	0·4168	38·695	24·631	1·3635	0·7499	36·867

It will be noted that α rises to a maximum and then falls, the change being fairly rapid at the edge of the lens; it is for this reason that the last section was subdivided into four parts.

To construct the outline of the lens, lines are drawn from the centre of the light source, making the angles θ with the horizontal; from the points in which these lines intersect the vertical corresponding to the inner lens surface lines are drawn, making the angles φ with the horizontal.

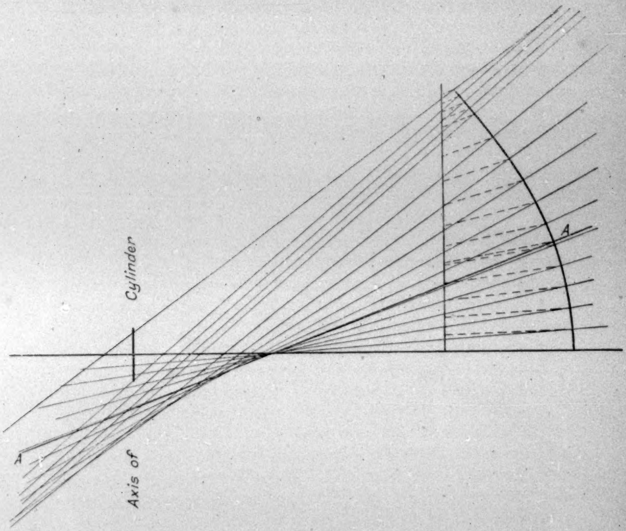

FIG. 3.

At a suitable point (determined by the minimum desirable marginal thickness for the lens) on the line inclined at φ_2, which represents the extreme ray, a straight line is drawn making an angle α_2 with the vertical; this will be a tangent to the surface. A point is taken on this tangent equidistant from the two refracted rays for which φ is 24·088 deg. and 24·631 deg., and a line drawn through it at the angle 39·910 deg. with the vertical: this will be the tangent to the surface where it meets the ray for which φ is 24·088 deg. Similarly, from the point on this tangent equidistant from the rays $\varphi=24{\cdot}088$ deg. and $\varphi=23{\cdot}544$ deg., another tangent is drawn at the angle 40·193 deg. with the vertical, and so on. Finally a curve is drawn to touch these tangents. The nature of the surface is most clearly indicated by drawing the normals at the points for which the calculations have been made. This has been done in Fig. 3, which illustrates the lens for which the calculations are given above. It will be noted that the part of the curve situated between the horizontal plane of symmetry and the line AA, which meets the surface where $\beta=5$ deg., and which therefore corresponds to uniform intensity in the refracted light, is of practically constant curvature and could be replaced by an arc of a circle without causing errors larger than are likely to be met with in manufacture. On going beyond this line, however, the curve rapidly becomes much flatter, being quite flat at some

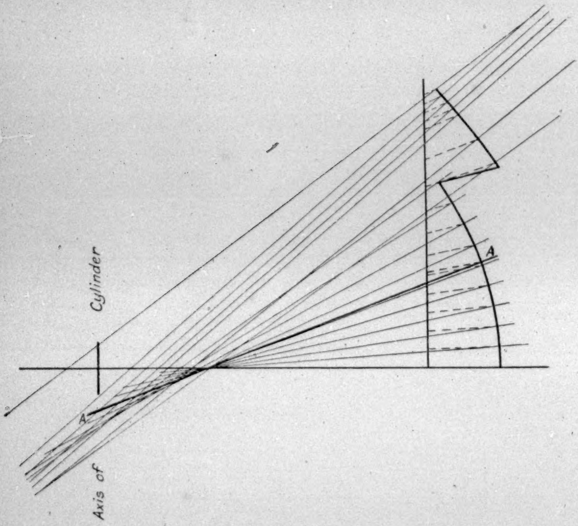

FIG. 4.

position for which β lies between 13 deg. and 14 deg., and beyond that the curvature changes sign. Owing to the continual change in curvature such a lens would probably be made with greater accuracy if cast from a very carefully made mould than if ground.

Fig. 4 shows the same design so modified that the maximum thickness is rather less than half that shown in Fig. 3. The flat surface separating the central lens from the dioptric element is shown making such an angle with the horizontal that no light will be stopped, rays just entering the dioptric element from the top of the light source (the actual height of which is 16 mm.) being inclined at a greater angle with the horizontal, and rays from the bottom of the source which are refracted in to the air at the entrance edge of the central lens being inclined at a less angle with the horizontal than the lower edge of the dioptric element.

In consequence of the neglect of differences in the loss of light at different parts of the lens, due to reflection and absorption, there are likely to be slight divergencies of the light distribution from that shown in Fig. 1. These, however, will probably be very small compared with the errors present in the mould when the first lenses are cast, so that any corrections that may be required can be easily effected in the removal of the faults in the mould. In cases where the angles of deviation are appreciably larger than in the present example it may be necessary to apply a correction to the first calculations to compensate for the differences in the losses caused by reflection and absorption.

It is desirable to make sure that the distribution of the light will not be affected appreciably when the size of the light source is taken into account. The exact mathematical treatment of the general problem is troublesome, but any particular case is readily dealt with by calculating, for a small linear source placed vertically on the axis at a suitable distance above or below the plane of symmetry, the angles with the horizontal and vertical made by rays from this source before and after refraction. It is convenient to exhibit the results of such calculations by plotting sin θ against β as independent variable, where θ is the complement of the inclination of the ray to the light source before refraction, and β is the angle between the emergent ray and the plane of symmetry of the lens. The general character of the result obtained is indicated in Fig. 5, which gives the approximate distribution from a small linear element 10 mm. from the flame centre—*i.e.*, 2 mm. outside the flame. Such a figure is most readily constructed by dividing up the useful energy produced by the element of the lamp which is being considered into a large number of equal parts, and finding the values of β which correspond to rays dividing these portions from one another. The erection on these segments of the β base of a number of equal rectangles gives an approximation to the required result. If the light source is symmetrical the corresponding element of the source on the opposite side of the median plane will give a distribution curve which is the reflection of the first, as shown by the lighter outline in Fig. 5. The distribution curve due to both of these elements, shown by a dotted curve, is obtained by taking a mean between the two previous curves. A comparison of this mean with the central distribution curve, which is chain dotted in the diagram, will indicate the direction and approximate amount of the corrections, if any, that are necessary.

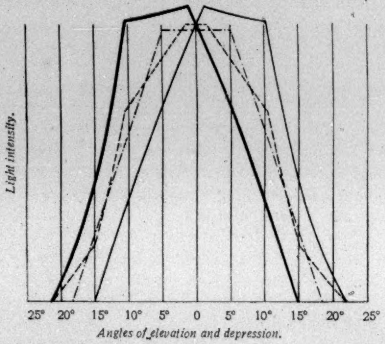

FIG. 5.

ABSTRACT.

The principle on which lenses for securing a required distribution of light from a given source have been designed is illustrated by a two-dimensional example. The principle employed is to divide the incident and emergent energy into a number of equal parts, and compute the lens system so that the rays which separate off these portions of incident light from one another are refracted as rays which separate the corresponding portions of the emergent light.

The surfaces obtained are in general of varying curvature, and the lenses must, therefore, be moulded. It is shown how the effect of the finite size of the light source may be determined.

DISCUSSION

Mr. R. S. **Whipple** asked how the results obtained with lamps designed on the lines discussed in the Paper compared with those previously employed, which had been evolved, he presumed, simply by the survival of the fittest? Were lenses of this type used as first cast or were the surfaces finally worked?

Mr. **Smith** stated in reply that the lamps previously in use gave very unsatisfactory results. Their performances varied greatly among themselves, and there did not appear to be any principle underlying their design. In many cases the lenses were not even symmetrically made, and the number of dioptric elements employed depended entirely on the whim of the maker. Some of these lenses had been ground, but he was not aware that they had been used except by the Admiralty. The new lenses, on the other hand, were giving very satisfactory results, despite the fact that some manufacturers had not yet quite realised the ideal conditions. The lenses were moulded and then, in some cases, glazed by what he believed was a secret process.

XXI. *The Choice of Glass for Cemented Objectives.* By T. Smith, *B.A.* (*From the National Physical Laboratory.*)

Received April 1, 1916.

It is well known that a telescope objective consisting of two component lenses can be so constructed as to be simultaneously free from chromatic and spherical aberrations and from coma, provided proper forms are given to the components. When these are to be cemented together the three conditions can only be satisfied if a careful choice is made of the kinds of glass used. Tables* have been published giving all the particulars necessary for the construction of such objectives when the corrections are required for an object at infinity. The present note deals with the changes in the kinds of glass to be employed when the objective is required to be free from these aberrations for objects at some finite distance.

The necessity for a change in the kinds of glass to be employed is readily demonstrated. The conditions† to be satisfied for freedom from spherical aberration and coma for magnification m (negative for an inverted image) are

$$A-m(3B+1)+m^2(3C+\varpi)-m^3B'=o,$$

and $$B-m(3C+\varpi)+m^2(3B'+1)-m^3A'=o.$$

When the objective is thin, these conditions reduce to

$$B'-B=\frac{1+m}{1-m}(2+\varpi) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and $$4C+2\varpi+1=\left(\frac{1+m}{1-m}\right)^2(5+2\varpi). \quad . \quad . \quad . \quad (2)$$

in consequence of the identical relations connecting the aberration coefficients. In the reduction the factor $1-m$ which occurs in both conditions has been rejected.

In an objective of the kind considered the only way in which the aberration coefficients can be varied, apart from a change in the kinds of glass used, to meet the different conditions when m is altered is by bending the lens as a whole. The changes in the coefficients consequent on such bending can be expressed in the form

$$B'-B=B'_0-B_0+2r(1+\varpi),$$

and $$C=C_0+r^2(1+2\varpi),$$

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* Gleichen: "Lehrbuch der Geometrischen Optik," p. 323.

† For notation employed *see* "Notes on the Calculation of Thin Objectives," "Proc." Ph. Soc., Vol. XXVII., p. 485.

where B_0, B'_0, C_0 and ϖ are constants depending only on the kinds of glass employed and r is a variable indicating the extent to which the objective is bent. The substitution of these expressions for $B'-B$ and C in equations (1) and (2) gives

$$B'_0-B_0+2r(1+\varpi)=\frac{1+m}{1-m}(2+\varpi), \quad . \quad . \quad . \quad (3)$$

and

$$4C_0+2\varpi+1+4r^2(1+2\varpi)=\left(\frac{1+m}{1-m}\right)^2(5+2\varpi). \quad . \quad (4)$$

If, now, $(1+\varpi)^2:(2+\varpi)^2=1+2\varpi:5+2\varpi$ it would be possible to employ the same two kinds of glass to give a cemented doublet having the desired corrections for various magnifications. In fact, however,

$$(5+2\varpi)(1+\varpi)^2-(1+2\varpi)(2+\varpi)^2=1,$$

and thus the necessary condition can never be satisfied.

Equations (3) and (4) show that there are in general two magnifications for which there will be no spherical aberration and no coma with two given kinds of glass. The solutions may be written in the form :—

$$\frac{1+m}{1-m}=\pm(1+\varpi)\sqrt{(B'_0-B_0)^2(5+2\varpi)(1+2\varpi)+4C_0+2\varpi+1}$$
$$-(B'_0-B_0)(1+2\varpi)(2+\varpi),$$

and

$$2r=\pm(2+\varpi)\sqrt{(B'_0-B_0)^2(5+2\varpi)(1+2\varpi)+4C_0+2\varpi+1}$$
$$-(B'_0-B_0)(5+2\varpi)(1+\varpi).$$

These formulæ are readily applied to any system when B_0, B'_0, C_0 and ϖ are known. When these have not been calculated for a combination of two glasses the formulæ may with advantage be expressed differently. Using a notation already explained* $B'-B$ and C may be put into the forms

$$B'-B=\frac{x-y}{1+2\varpi}+\frac{1+\varpi}{1+2\varpi}\{2r(1+2\varpi)+3y-(K-K')(3+2\varpi)\}, \quad (5)$$

and

$$C=KK'(R+R'+1)^2-KK'(1+2\varpi)+(KR-K'R')^2$$
$$+r\{3y-(K-K')(3+2\varpi)\}+r^2(1+2\varpi)$$
$$=-\frac{1+2\varpi}{4}+KK'(R+R'+1)^2+\frac{x^2}{4}-\frac{5+2\varpi}{4(1+2\varpi)}(x-y)^2$$
$$+\frac{1}{4(1+2\varpi)}\{2r(1+2\varpi)+3y-(K-K')(3+2\varpi)\}^2, \quad (6)$$

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* *See* "Thin Objectives," p. 489, equation (3).

where $$y=K(1+R)-K'(1+R')$$

and $$x=K-K'+y\varpi.$$

It at once follows that

$$(B'_0-B_0)(1+2\varpi)=x-y,$$

and that

$$(B'_0-B_0)^2(5+2\varpi)(1+2\varpi)+4C_0+2\varpi+1=x^2+4KK'(R+R'+1)^2.$$

The magnifications for which the corrections can be made are, therefore, given by

$$\frac{1+m}{1-m}=\pm(1+\varpi)\sqrt{x^2+4KK'(R+R'+1)^2}+(2+\varpi)(y-x), \quad (7)$$

and the corresponding curvatures of the cemented surface are

$$y+\tfrac{1}{2}(2+\varpi)\{\pm\sqrt{x^2+4KK'(R+R'+1)^2}-x\}. \quad . \quad . \quad (8)$$

Formulæ (7) and (8) are in a convenient form for numerical use. To determine suitable combinations of glasses for various distances two refractive indices may be selected and the calculations performed for varying values of K and K'. When a set of values corresponding with the available range of optical glasses has been thus determined one of the refractive indices may be altered and a fresh set of values obtained. The results of series of these calculations in which one of the refractive indices is constant throughout are conveniently plotted in two dimensions, with the other refractive index and the ratio of the powers of the component lenses as the variables for Cartesian co-ordinates. Contours for which m has a constant value can be drawn in the chart by interpolation among the values obtained from the calculations for the two dimensional series of points in exactly the same way as contours are drawn from field observations in surveying. Instead, however, of marking off lengths in one direction in proportion to $-K/K'$, it is more convenient to make them proportional to $\log(-K/K')$. By so doing it becomes possible, when a series of charts such as has just been described has been constructed, to find in a few minutes whether any combination of two glasses out of the many kinds which may be available will enable the required conditions to be satisfied. For it is only necessary to prepare on translucent paper a chart of these glasses taking as ordinates and abscissæ their values of μ and log ν, — the μ referring to the wave-length for which correction is required, and the ν being calculated for the wave-lengths for which the focal lengths are to be equal—on the same scale as that used in plotting refractive indices and $\log(-K/K')$ in the contour maps. The glass chart is then placed over one of these maps with the corresponding lines μ=constant superposed. Let each available glass of the refractive index for which the particular map was constructed be brought in turn over the point for which $\log(-K/K')=0$. If in any case the contour for the desired magnification passes through the point representing another glass, the glass thus obtained when combined with that for which the two diagrams are adjusted will give a cemented objective having the desired correction. The justification for thus using the two diagrams after the manner of a slide rule lies in the relation $-K/K'=\nu/\ '$ whence $\log(-K/K')=\log\nu-\log\ '$.

In constructing these contour maps much time may be spent fruitlessly in making calculations for points which only give imaginary values for m. This may be avoided by first of all plotting the curve which separates the regions where the roots are imaginary from those where they are real. From equation (7) this boundary is given by

$$x^2+4KK'(R+R'+1)^2=0\ ;$$

i.e., the boundary consists of the two curves

$$x=2(R+R'+1)\sqrt{-KK'} \quad . \quad . \quad . \quad . \quad (8)$$

and

$$x=-2(R+R'+1)\sqrt{-KK'} \quad . \quad . \quad . \quad (9)$$

Suppose that μ, K and K' are given. These equations then serve to determine μ'. The solution presents no difficulties, as x involves μ' only to the second order and R' involves it to the first order. The equations are, therefore, quadratic in μ', and the boundary is traced out by solving these for a series of values of K and K'. Fig. 1 gives a general view of the part of the boundary in the neighbourhood of the origin when one refractive index is 1·5 and Fig. 2 is drawn for refractive index 1·6. Each of these diagrams in reality contains the results of calculations for two separate cases, those parts above the line

$\log(-K/K')=0$, relating to systems in which the lens of fixed index is the negative component, and those below this line to systems in which it is the positive component. The two are conveniently included together in the one diagram, as the

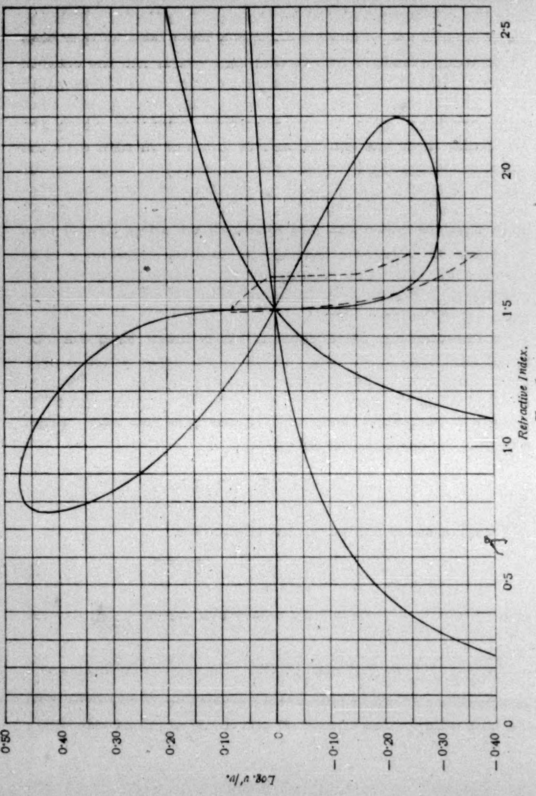


FIG. 1.

boundaries in the one case are the natural continuations of those in the other.

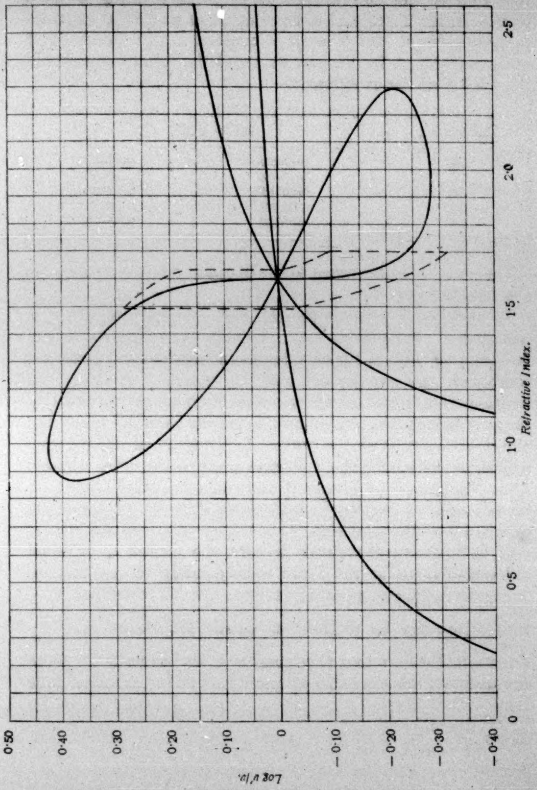


Fig. 2.

The curve given by equation (8) is closed and resembles a written figure 8 in shape. The branch in the upper part of the diagram is longer than that in the lower, and both loops decrease in size as the fixed refractive index is increased. The curve of equation (9) consists of two branches which are asymptotic to $\mu=0$ and pass through the point representing the fixed glass. In the upper part of the map there are two asymptotes perpendicular to the lines $\mu=$ constant. The positions of these asymptotes for various values of the refractive index of the fixed glass are as follows :—

Fixed index.	$\log(-K/K')$	
1·4	0·11362	0·37359
1·5	0·10694	0·32453
1·6	0·10102	0·28728
1·7	0·09575	0·25791
1·8	0·09102	0·23407

There are other branches to the boundary, but they are of no practical interest.

To distinguish between the real and imaginary regions it is sufficient to take a single case. Let the two refractive indices be equal, so that, so far as spherical aberration and coma are concerned, the two glasses may be regarded as one. The magnifications for which there is correction are then μ and $1/\mu$, the lens taking the well-known meniscus form in which the object or image is at the centre of curvature of one surface, which coincides with the aplanatic point of the other surface. Thus the line $\mu=\mu'$ is one of the contours which are to be traced, and the regions in which this line lies are those for which real solutions exist.

It is not very convenient to plot the contours for equal differences in m, as the range corresponding to real images, or negative values of m, goes from 0 to $-\infty$. The contours may with advantage be plotted for equal differences in $\dfrac{1+m}{1-m}$. Equation (7) shows that this quantity is always finite for finite curvatures of the lens surfaces, and it has the further advantage that the substitution for m of its reciprocal merely alters the sign of $\dfrac{1+m}{1-m}$, so that for a given magnification one contour gives the case of a lens with the crown component leading, and the corresponding contour of opposite sign gives a lens with the flint component leading. The range of values through which this quantity goes for all real images is from -1 through zero to +1. The following table will be found useful in making use of the charts :—

TABLE 1.

Value of $\frac{1+m}{1-m}$	Value of m.	Value of $\frac{1+m}{1-m}$	Value of m.
0·00	−1	0·55	−0·29032
0·05	−0·90416	0·60	−0·25000
0·10	−0·81818	0·65	−0·21212
0·15	−0·73913	0·70	−0·17647
0·20	−0·66667	0·75	−0·14286
0·25	−0·60000	0·80	−0·11111
0·30	−0·53846	0·85	−0·08108
0·35	−0·48148	0·90	−0·05263
0·40	−0·42857	0·95	−0·02564
0·45	−0·37931	1·00	0
0·50	−0·33333		

The dotted outlines in Figs. 1 and 2 indicate approximately the area that can be covered on the contour maps by the kinds of optical glass that have so far been manufactured when the glass chart is given as great a movement parallel to the lines $\mu =$ constant as the range of glass allows. Obviously the regions of most interest are those between the infinite branches and the figure of eight projections through which the line $\mu = \mu'$ runs. The principal features of the contours in these parts can be ascertained with some probability of accuracy from simple general reasoning.

For this purpose it is convenient to consider an analogous case in which the conditions can be readily visualised. Suppose, then, that the conditions are expressed in terms of the more familiar case of surveying. Horizontal distances in two directions at right angles—say, North and South, East and West—take the place of μ and $(-K/K')$ respectively. Heights will be the analogue of values of $\frac{1+m}{1-m}$. The case is not, however, quite that of an ordinary survey, for there are two vertical distances involved. Imagine, then, that the charts relate to a cave, the one height being that of the roof, the other that of the floor. The regions where the roots are imaginary correspond with solid rock, where there is neither roof nor floor. The curve separating the real and imaginary regions gives the horizontal extension of the cave, the walls of which at points on the curve are vertical. In this particular case we also know that, along the North and South line through the extremity of the recess, the height of the roof and the depth of the floor from the datum level are constant and equal. Thus if a number of East and West vertical sections are projected in a North and South direction and drawn superimposed on one another they will intersect in two points, the heights of which will be—taking the case of refractive index 1·5 for instance—plus and minus five. The contours with which we are most concerned are plus and minus one and those between these. Clearly there must be points on these contours between the line $\mu=1\cdot5$ and the walls on either hand. As the sections are taken nearer to the closed end of the cave the wall which becomes tangential to the plane of constant height will become flatter, the level at which it is perpendicular tending to the contour of zero height.

It would be expected that with the falling width of the cave and the increased steepness of the walls the maximum height of the cave would increase, and that at the extremity the opening would become a vertical line of infinite length. Nothing can be said as to the level at which the walls of the infinite branch are vertical.

It is evident that all the contours which are of more practical importance pass through the line extremity of the cave and emerge through the corresponding opening opposite, and that they tend to crowd together as the cave becomes more confined in width. In those parts where the walls are vertical somewhere between the contours plus and minus one the contours for all negative magnifications will tend to be close together, so that a change in the kinds of glass may not be necessary in practice.

It is reasonable to suppose that the level at which the wall running nearly North and South is vertical will gradually change from zero height, which it should have near the extreme end, to appreciably different levels in the more open parts. The various contours will thus touch the curve on the plan marking the extreme horizontal extent of the cave. On one side of these points of contact the contours will lie below the perpendicular part of the wall, and on the other side they will be above it. The shape of the extreme boundary evidently serves as an approximate indicator of the shape of the contours close to the wall, but nothing can be said without detailed calculations of the directions the contours will take when the projecting bluff of rock has been passed.

Reference to the diagrams shows the general features to which this reasoning leads. Fig. 3 shows for $\mu=1\cdot5$ a number of vertical sections of that part of the cave which lies to the right of the plane $\mu=\mu'$ by planes which have the values of log ν'/ν given in the diagram. The contours for which $\frac{1+m}{1-m}=+1$, 0 and -1 derived from these sections are given in Fig. 4. The curve on the right, which is hardly distinguishable from the contour $\frac{1+m}{1-m}=-1$ is the boundary between real and imaginary regions. The figures on the right of this boundary give the contours which touch the boundary at the positions indicated. The contours for real images appear very close together, so much so that it is natural to inquire whether the same kinds of glass will not in practice give, for any negative magnification, an objective indistinguishable from one made of the theoretically necessary glasses notwithstanding the mathematical impossibility. To decide this point a special case may be considered. With a given pair of glasses let the magnifications for which correction is theoretically perfect be m' and m''. Let an objective be made from these which gives no coma at magnification m, the lens itself acting as stop. The condition for this is

$$B'-B=\frac{1+m}{1-m}(2+\varpi).$$

The amount of spherical aberration is then measured by

$$\tfrac{1}{4}\left\{4C+2\varpi+1-\left(\frac{1+m}{1-m}\right)^2(5+2\varpi)\right\}.$$

This may be shown to be equal to

$$-\frac{1}{4(1+\varpi)^2}\left(\frac{1+m}{1-m}-\frac{1+m'}{1-m'}\right)\left(\frac{1+m}{1-m}-\frac{1+m''}{1-m''}\right).$$

From the diagram a case may be selected at random : a possible combination is

$$\frac{1+m'}{1-m'}=1,\quad \frac{1+m''}{1-m''}=-3.$$

If a lens were made from these glasses in the way suggested for $m=-1$, the spherical aberration would amount to about 0·26, a value which cannot be neglected for many purposes. It may be concluded that although the same two glasses can be satisfactorily used for a fair range of magnifications, it will for some purposes be necessary to secure glasses which lie on the theoretical curve well within the limits of the extreme curves for real images.

When the two conditions cannot be satisfied, and it is decided to satisfy one which will give two roots and keep the amount of the second aberration as small as possible, it is desirable if the second glass is taken from the real region to keep as close as possible to the boundary which separates the real from the imaginary regions, as otherwise the roots for

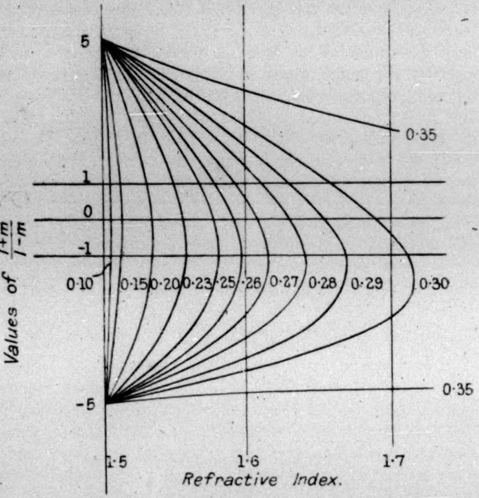


Fig. 3.

the selected glasses may prove to be imaginary. This is readily seen on considering the case of spherical aberration. When both glasses have the same refractive index it is impossible to secure freedom from spherical aberration for any negative magnification. There must, therefore, be a region in the cave in which the spherical aberration condition leads to imaginary roots for real images. The boundary to this region is in fact close to the boundary of the imaginary region with which we have been dealing, and the contours that are traced on the

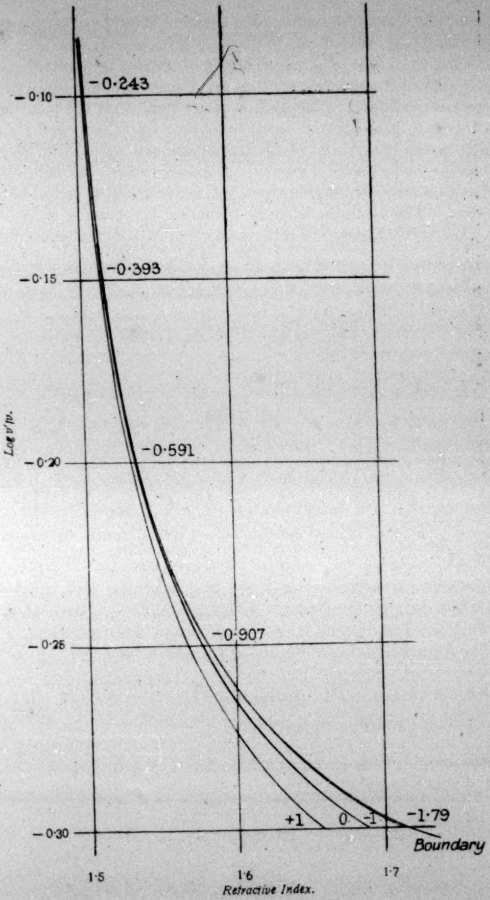

-0·243
-0·393
-0·591
-0·907
-1·79
+1
0
-1
Boundary
- 0·10
- 0·15
- 0·20
- 0·25
- 0·30
Log ν'/ν.
1·5
1·6
1·7
Retractive Index.

Fig. 4.

charts necessarily lie in the space between these two imaginary regions.

When the kinds of glass necessary to secure the corrections with sufficient accuracy are not available, a triple objective becomes necessary. The author has shown* that the solution in this case also depends upon quadratic equations, and thus there is the possibility of finding imaginary roots with such lenses as well as with doublets. A case in which the solution fails is obtained by taking equal refractive indices for the two glasses. The formulæ already obtained are readily applied to this further case. From equations (6) of the previous investigation it is clear that $\mathbf{B}'_0-\mathbf{B}_0$ is a linear, and $\mathbf{C}_0$ a quadratic function of θ. Consider the functions f_1 and f_2 where

$$f_1=\mathbf{B}'_0-\mathbf{B}_0-(B'_0-B_0)(1-2\theta)$$

and

$$f_2=(4\mathbf{C}_0+2\varpi+1-A')-(4C_0+2\varpi+1-A')(1-2\theta)^2.$$

When $\theta=0$, the relations $\mathbf{B}'_0-\mathbf{B}_0=B'_0-B_0$ and $\mathbf{C}_0=C_0$ must hold. When $\theta=1$, the necessary relations are $\mathbf{B}'_0-\mathbf{B}_0=-(B'_0-B_0)$ and $\mathbf{C}_0=C_0$. When $\theta=\frac{1}{2}$ from symmetry $\mathbf{C}$ is a minimum, *i.e.*, $\mathbf{C}=\mathbf{C}_0$, and $\mathbf{B}_0=\mathbf{B}'_0$. In such a symmetrical system it is not difficult to prove that $4\mathbf{C}+2\varpi+1=A'$ where the A' relates to one-half of the system as actually combined with a similar lens to produce the compound system. It follows that $f_1=f_2=0$ when $\theta=0$, $\frac{1}{2}$ and 1 and hence f_1 and f_2 are always identically zero.

The equation giving m in terms of θ is evidently

$$\frac{1+m}{1-m}=\pm(1+\varpi)\sqrt{(1-2\theta)^2\{(B_0'-B_0)^2(5+2\varpi)(1+2\varpi)+4C_0+2\varpi+1-A'\}+A'}$$
$$-(B_0'-B_0)(1-2\theta)(1+2\varpi)(2+\varpi).$$

Rearranging this as an equation for θ in terms of m it is found that θ is real if

$$\left(\frac{1+m}{1-m}\right)^2\{(B_0'-B_0)^2(1+2\varpi)(5+2\varpi)+4C_0+2\varpi+1-A'\}$$
$$-A'\{(B'_0-B_0)^2(1+2\varpi)+(4C_0+2\varpi+1-A')(1+\varpi)^2\}$$

---

* "Thin Objectives," p. 495.

is positive. Over the range of suitable glasses for objectives the spherical aberration is positive for parallel incident light when the first surface is plane; that is to say, A' is positive, and since the region within which

$$(B_0'-B_0)^2(1+2\varpi)(5+2\varpi)+4C_0+2\varpi+1$$

is negative is that in which triple objectives are likely to prove most useful, the triple form will first break down when $\frac{1+m}{1-m}=1$. When the two refractive indices are equal $B_0=B'_0$ and $4C_0+2\varpi+1=A'$, so that the above quantity is zero. When the difference between the refractive indices is small, it has a positive value if the refractive index of the less dispersive medium is less than that of the more strongly dispersive medium, and is negative if the reverse is the case. Thus one region in which the triple solution breaks down is within the cave, and bounded by the line $\mu=\mu'$, the region lying on that side of this line which is not practically important. It is not difficult to verify that on the other side of this line no imaginary region is reached until the area which can be covered by useful optical glasses is passed. Thus the triple form of objective can be employed in any practical case in which the available kinds of glass do not enable a satisfactory cemented doublet to be made.

It may be noted that the contours giving the kinds of glass for which the two conditions are satisfied can be used for other purposes. For example, in a doublet lens they mark off the region where the one aberration is positive from that in which it is negative when the second aberration is removed. In triple lenses they separate the region where the two lenses of one kind of glass are of the same sign from that in which they are of different signs for one form of solution. Other uses to which they can be put readily suggest themselves in various problems which are encountered in the course of designing optical instruments.

TABLE II.

$\log \nu/\nu'$	K.	K'.
0·05	9·1955	−8·1955
0·10	4·8621	−3·8621
0·15	3·4240	−2·4240
0·20	2·7097	−1·7097
0·25	2·2849	−1·2849
0·30	2·0048	−1·0048
0·35	1·8073	−0·8073
0·40	1·6614	−0·6614

The author desires in conclusion to express his indebtedness to Miss Dale, Mr. Trump and Mr. Bell for their assistance in the calculations from which the contours have been plotted.

ABSTRACT.

The strict fulfilment of the mathematical conditions for freedom from colour, spherical aberration and coma, for objects at varying distances from a thin cemented doublet lens, necessarily demands a change in the kinds of glass as the position of the object is changed. The Paper describes a method by which the proper glasses can be determined by using a glass chart on translucent paper, in conjunction with diagrams calculated for the purpose, as a slide-rule. With most glasses the solution to the problem is imaginary, and formulæ are given for calculating the boundary separating real and imaginary solutions by solving a quadratic equation. In practice it is found that the curves for all real images lie very close to one another. Notwithstanding this, a numerical example shows that there will be a perceptible difference in the definition obtained if in place of the theoretically necessary type a kind of glass is substituted which does not differ greatly from the other, and lies on a curve giving perfect correction for another real magnification. It is further shown that when no real solution is forthcoming for a double lens a real solution will in practice be obtained by adopting a triple objective made of the same glasses.

XXII.—*The Correction of Chromatic Aberrations when the External Media are Dispersive.* By T. SMITH, *B.A.* (*From the National Physical Laboratory.*)

RECEIVED APRIL 1ST, 1916.

SUMMARY.

WHEN one of the external media of a lens system is dispersive it is not possible to ensure the absence of differences in the size and position of images of all objects formed by light of different wave-lengths. The degree to which correction can be carried is investigated, and formulæ are given by which the power and position of the external surfaces of a system can be found when the type of correction to be adopted is given.

1. IT will be convenient to denote the four quantities which determine the behaviour of the paraxial rays in the optical system by the letters A, B, C, D. The power of the system will be denoted by A; B and C determine the position of the extreme lens surfaces relatively to the cardinal points of the system; for a thin system D is zero. The standard relation connecting these four quantities will be taken as $BC-AD=1$.

If the refractive indices of the first and last media be μ and μ', the distances from the first and last refracting surfaces of the conjugate points for which the magnification is N, will be x and x', where

$$x=-\frac{\mu}{A}\left(B-\frac{1}{N}\right),$$

and

$$x'=\frac{\mu'}{A}(C-N),$$

both distances being measured from the surfaces in the direction from the first to the last surface.

The conditions for complete colour correction (*i.e.*, no colour differences in the size and position of the image of any object) are that B, C, and the ratios $\mu:\mu':A$ should be independent of the colour of the light.

2. If only one external medium is dispersive these conditions cannot all be satisfied. Under these circumstances it may be shown that a thin system will not form an image of any object of finite size free from colour. Putting the conditions down generally we find the change of magnification given by

$$\frac{\delta N}{N}=(1-N)\left\{\frac{\delta\mu}{\mu}-\frac{\delta A}{A}\right\}. \quad . \quad . \quad . \quad (1)$$

The separation of the images is equal to

$$\frac{\mu'(1-N)}{A}-\frac{(\mu'+\delta\mu')(1-N-\delta N)}{A+\delta A}$$

$$=\frac{\mu'(1-N)}{A}\left\{-\frac{\delta\mu'}{\mu'}+\frac{\delta A}{A}+\frac{\delta N}{1-N}\right\}$$

$$=\frac{\mu'(1-N)}{A}\left\{\frac{\delta\mu}{\mu}-\frac{\delta\mu'}{\mu'}-\frac{\delta N}{N}\right\} \quad . \ . \ . \ . \ . \ . \quad (2)$$

by (1). Thus the position and magnification with a thin system cannot be the same for two colours unless the external refractive indices are proportional for the two colours, proving the result stated above.

3. Equation (2) shows that the inconsistency of the two-colour conditions when one medium is dispersive and the other is not, is of such magnitude as to render a thin system quite unsuitable for all practical purposes.

4. The next simplest arrangement to a thin system is two thin systems separated by air. In this case D is independent of colour. The solution to which the conditions for both corrections for magnification N lead is

$$\frac{\delta A}{A}=\frac{C}{C-N}\,\frac{\delta\mu}{\mu}+\frac{NB}{NB-1}\,\frac{\delta\mu'}{\mu'} \quad . \ . \ . \ . \ . \ . \quad (3)$$

$$\delta B=\frac{NB-1}{C-N}\,\frac{\delta\mu}{\mu}+B\frac{\delta\mu'}{\mu'} \quad . \ . \ . \ . \ . \ . \quad (4)$$

$$\delta C=C\frac{\delta\mu}{\mu}+\frac{C-N}{NB-1}\,\frac{\delta\mu'}{\mu'} \quad . \ . \ . \ . \ . \ . \quad (5)$$

obtained by putting $\delta x=\delta N=0$ in the equations of the first paragraph. These results may be verified by noting that they satisfy

$$B\delta C+C\delta B-(BC-1)\frac{\delta A}{A}=0$$

showing that $\delta D=0$, and by substituting the values of the differentials in the formulæ for the differences in size and position of the images of an object placed so that the magnification for one of the two colours considered is N'. The results so obtained are

$$\frac{\delta N'}{N'}=(N'-N)\left\{\frac{1}{C-N}\,\frac{\delta\mu}{\mu}+\frac{B}{NB-1}\,\frac{\delta\mu'}{\mu'}\right\}$$

and $$\delta x' = \frac{\mu'(N'-N)}{A}\left\{\frac{C-N'}{C-N}\,\frac{\delta\mu}{\mu} - \frac{N'B-1}{NB-1}\,\frac{\delta\mu'}{\mu'}\right\}$$

$$= \frac{\mu'(N'-N)}{A}\left\{\frac{\delta\mu}{\mu} - \frac{\delta\mu'}{\mu'} - \frac{\delta N'}{N'}\right\}$$

a result which corresponds exactly with (2) when $N=1$.

5. The more general case of correction for magnification N when D is not restricted to be independent of the colour may be investigated as follows :—

Write the fundamental equations in the form,

$$x = -\frac{\mu D}{AD}\left(B - \frac{1}{N}\right)$$

and $$x' = \frac{\mu' D}{AD}(C-N).$$

Then $$B = \frac{1}{N} - x\frac{AD}{\mu D}$$

and $$C = N + x'\frac{AD}{\mu D},$$

so that $AD = BC - 1 = \left(\frac{1}{N} - x\frac{AD}{\mu D}\right)\left(N + x\frac{AD}{\mu' D}\right) - 1,$

or since in general both A and D are finite

$$AD + \frac{N}{x'}\mu' D - \frac{1}{Nx}\mu D + \frac{\mu D \,.\, \mu' D}{xx'} = 0.$$

Differentiate this applying the conditions

$$\delta x = \delta x' = \delta N = 0.$$

Then $$\delta(AD) = \left(\frac{1}{N} - \frac{\mu' D}{x'}\right)\frac{\delta(\mu D)}{x} - \left(N + \frac{\mu D}{x}\right)\frac{\delta(\mu' D)}{x'}$$

or $$\frac{\delta(AD)}{AD} = \frac{C}{C-N}\,\frac{\delta(\mu D)}{\mu D} + \frac{NB}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}. \quad . \quad . \quad (6)$$

Now differentiate the expressions for B and C applying the same conditions as before, and substituting from (6) for $\delta\,(AD)$. The results

$$\delta B = \frac{NB-1}{C-N}\,\frac{\delta(\mu D)}{\mu D} + B\frac{\delta(\mu' D)}{\mu' D}. \quad . \quad . \quad . \quad . \quad (7)$$

and
$$\delta C = C\frac{\delta(\mu D)}{\mu D} + \frac{C-N}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}. \quad . \quad . \quad . \quad . \quad (8)$$
immediately follow.

It will be observed that equations (6), (7) and (8) are derived from (3), (4) and (5) by writing AD, μD, and $\mu' D$ in all cases for A, μ and μ' respectively. In this more general case we shall thus have

$$\frac{\delta N'}{N'} = (N'-N)\left\{\frac{1}{C-N}\,\frac{\delta(\mu D)}{\mu D} + \frac{B}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}\right\}$$

and
$$\delta x' = \frac{\mu' D(N'-N)}{AD}\left\{\frac{C-N'}{C-N}\,\frac{\delta(\mu D)}{\mu D} - \frac{N'B-1}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}\right\}$$

$$= \frac{\mu'(N'-N)}{A}\left\{\frac{\delta\mu}{\mu} - \frac{\delta\mu'}{\mu'} - \frac{\delta N'}{N'}\right\} \text{as before.}$$

6. The result involving the quantity $\frac{\delta\mu}{\mu} - \frac{\delta\mu'}{\mu'} - \frac{\delta N'}{N'}$, which thus holds in all cases, might have been written down at once from the consideration that the ratio of the distance between two image points on the axis to the distance between their conjugates is μ'/μ times the product of the transverse magnifications for the two points. Taking one of these points as that for which the two chromatic aberrations are corrected, the preceding result at once follows. The unsuitability of thin lens systems follows from the fact that the position for which the aberrations are corrected is that occupied by the lens itself.

7. An interesting case is obtained when $N=0$. Equations (6) and (8) then reduce to A/μ=constant and $C\mu'/\mu$=constant. In other words, the focal length in the dispersive medium in which the rays are parallel is to be constant, and the rays of different colours incident parallel to the axis at any given point of the first refracting surface are to meet the last surface at distances from the axis proportional to the ratio of the refractive index of the first to that of the final medium for their respective colours. The chromatic conditions will thus be satisfied by choosing the position of the last surface to suit one condition and adjusting its power to satisfy the other.

8. As another example the case of the system considered in 4, with air as the final medium, may be taken. Equation (5) gives C/μ=constant, showing that the type of correction required by the first system is independent of the magnification for which the whole is to be used. It would therefore be

5

possible in this case to substitute in the same position different thin lenses for the second system, and obtain correction for various positions of the object. If t be the axial separation of the two groups the conditions are satisfied by making the power of the first system equal to $(1-\mu p)/t$, and of the second to $\frac{1}{t}+\frac{1}{x'}-\frac{1}{\mu p}\left(\frac{1}{t}+\frac{N}{x'}\right)$, where p has the same value for different colours. The power for the complete system is $(\mu p-N)/x'$.

The power of the first system may be written in the form $\frac{1-p}{t}+\frac{(1-\mu)p}{t}$ showing that if this lens would be itself rendered achromatic by replacing the dispersive external medium by air, and if the ratio of the radius of curvature of the first surface to the focal length of the lens in air be $(1-p)/p$, the lens will be properly corrected for this purpose, whatever the nature of the first medium with which it is actually used. In particular, such a lens could be used in conjunction with suitable second systems for the formation of the images of objects in dispersive liquids. Since p is not subject to any limitations it is evident that any achromatic lens may be so used, and its value of p used to determine a suitable second system. A number of other interesting solutions can be readily obtained. Any practical case can be quickly worked out with the help of equations (6), (7) and (8).

9. When all the chromatic conditions cannot be satisfied it is not necessarily the case that the best corrections will be obtained by applying the conditions that the image should be fully corrected for some one magnification. Where a considerable range of magnifications is to be employed it may be preferable to have the images of various colours formed on the principal ray for the standard colour. The position of the stop will evidently enter into this condition. Let the stop be placed in such a position that its magnification for the complete lens is d. Then if the distances from the first and last surfaces of the stop and of its image are S and S', the relations

$$S=-\frac{\mu}{A}\left(B-\frac{1}{d}\right) \text{ and } S'=\frac{\mu'}{A}\,(C-d)$$

will be satisfied.

The conditions to be applied are evidently

$$\delta x=0 \text{ and } \frac{\delta x'}{x'-S'}=\frac{\delta N}{N}.$$

These lead to

$$-d\left\{\left(\frac{\delta\mu}{\mu}-\frac{\delta A}{A}\right)(NB-1)+N\delta B\right\}$$
$$=(C-N)\left(\frac{\delta\mu'}{\mu'}-\frac{\delta A}{A}\right)+\delta C=d\frac{\delta N}{N}. \qquad (9)$$

10. Equation (9) will be satisfied for all values of N if

$$d\left(\frac{\delta\mu}{\mu}-\frac{\delta A}{A}\right)=C\left(\frac{\delta\mu'}{\mu'}-\frac{\delta A}{A}\right)+\delta C,$$

and
$$\frac{1}{d}\left(\frac{\delta\mu'}{\mu'}-\frac{\delta A}{A}\right)=B\left(\frac{\delta\mu}{\mu}-\frac{\delta A}{A}\right)+\delta B,$$

which reduce to

$$S'\delta B=\delta(\mu'D)$$

and
$$-S\delta C=\delta(\mu D).$$

The differences in the size and position of the images of various colours are given by

$$\frac{\delta N}{N}=\frac{NB-1}{dB-1}\,\frac{\delta(\mu D)}{\mu D}-\frac{C-N}{C-d}\,\frac{\delta(\mu'D)}{\mu'D}=\frac{\delta x'}{x'-S'},$$

and object points are represented in the image plane for the standard colour by circles of diameter $\frac{\delta N}{N}$ times the diameter of the stop in the image space, with their centres at the image point for the standard colour.

11. This effect in the image plane for the standard colour may be compared with the corresponding results given by correcting according to equations (6), (7) and (8). In this case the diameter of the diffusion circles when the magnification for the standard colour is N', is

$$\frac{N'-N}{N'-d}\left\{\frac{C-N'}{C-N}\,\frac{\delta(\mu D)}{\mu D}-\frac{BN'-1}{BN-1}\,\frac{\delta(\mu'D)}{\mu'D}\right\},$$

or
$$\frac{A\delta x'}{\mu'(N'-d)}$$

times the diameter of the stop in the final medium, and the magnification in this plane determined by the centres of these circles is

$$1+\frac{N'-N}{N'-d}\left\{\frac{C-d}{C-N}\,\frac{\delta(\mu D)}{\mu D}-\frac{dB-1}{NB-1}\,\frac{\delta(\mu'D)}{\mu'D}\right\}$$

times that for the standard colour.

12. When equation (9) is only satisfied for the one magnification N the extra degree of freedom present may be taken into account by regarding $\frac{\delta N}{N}$ as an independent variable.

The equations for the changes in the focal length and position of the foci for different colours are then

$$\frac{\delta(AD)}{AD}=\frac{C}{C-N}\,\frac{\delta(\mu D)}{\mu D}+\frac{NB}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}+\frac{C-dNB}{(C-N)(NB-1)}\,\frac{\delta N}{N},$$

$$\delta B=\frac{NB-1}{C-N}\,\frac{\delta(\mu D)}{\mu D}+B\frac{\delta(\mu' D)}{\mu' D}-\frac{dB-1}{C-N}\,\frac{\delta N}{N},$$

$$\delta C=C\frac{\delta(\mu D)}{\mu D}+\frac{C-N}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}+\frac{C-d}{NB-1}\,\frac{\delta N}{N}.$$

When the magnification is N' for the standard colour the diffusion circles in this image plane will be of diameter

$$\frac{N'-N}{N'-d}\left[\frac{C-N'}{C-N}\left\{\frac{\delta(\mu D)}{\mu D}-\frac{dB-1}{NB-1}\,\frac{\delta N}{N}\right\}\right.$$
$$\left.-\frac{N'B-1}{NB-1}\left\{\frac{\delta(\mu' D)}{\mu' D}+\frac{C-d}{C-N}\,\frac{\delta N}{N}\right\}\right]$$
$$+\frac{(C-N')(BN'-1)(N-d)}{(C-N)(BN-1)(N'-d)}\,\frac{\delta N}{N}$$

times the diameter of the stop in the image space, and the magnification for the centres of these circles will be

$$1+\frac{N'-N}{N'-d}\left\{\frac{C-d}{C-N}\,\frac{\delta(\mu D)}{\mu D}-\frac{dB-1}{NB-1}\,\frac{\delta(\mu' D)}{\mu' D}-\frac{(C-d)(dB-1)}{(C-N)(NB-1)}\,\frac{\delta N}{N}\right\}$$

times that for the standard colour. The results of the preceding sections can be found from these formulæ by giving the appropriate values to $\frac{\delta N}{N}$.

The best way of correcting can be determined from the last two expressions on taking into consideration the range of magnifications for which the system is to be used, and the relative magnitudes of the field of view and the angular aperture.

XXIII. *Note on the Use of the Auto-Collimating Telescope in the Measurement of Angles.* By J. Guild, *A.R.C.S., D.I.C., F.R.A.S., from the National Physical Laboratory.*

Received April 1, 1916.

The purpose of this note is to draw attention to certain sources of error which exist in some of the methods commonly adopted for the optical determination of angles, and which have not, as far as the author is aware, been pointed out before.

As an example of this type of measurement consider the case in which it is desired to compare an angle under test (say, the right angle of a totally reflecting prism) with a standard angle of the same nominal value of which the error is known. There are several methods by which this may be accomplished, but the one which at first sight seems most attractive is the following :—

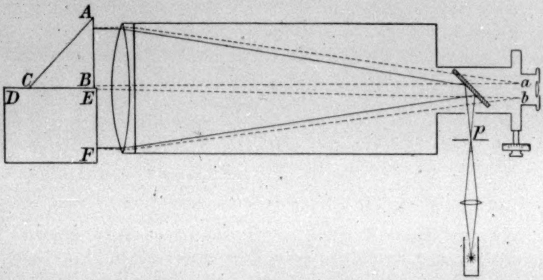


Fig. 1.

One face, B C, Fig. 1, of the prism is placed against the face D E of the block containing the standard angle DEF, and the surfaces are worked together until the interference fringes formed by the air film are as broad as possible and parallel to the edge B C. The inclination of A B to E F is then determined by means of some form of auto-collimator. The instrument which is employed at the Laboratory for measurements of this nature consists of an astronomical telescope of 3 in. aperture and 125 cm. focal length. A piece of unsilvered plane parallel glass, *m*, situated 5 or 6 cm. in front of the focal plane, serves to reflect light from a small illuminated pinhole, *p*, along the axis of the telescope.

The latter is first focussed on infinity and the position of *p* is then adjusted so that an optical flat placed in front of the objective and at right angles to the axis of the telescope returns the light to form an image of *p* in the focal plane of a Zeiss micrometer eyepiece. Reverting to Fig. 1 it is clear that if the planes A B and E F are not exactly parallel, two images *a* and *b*, will be formed, one from each plane. By gently tapping the prism with a pencil it can be rotated on the block until the line joining *a* and *b* is parallel to the traverse of the micrometer (initially adjusted to be approximately parallel to the edges A B and E F). The distance *a b* is then measured and converted into angle. From this and the known value of Ê the angle B can at once be deduced.

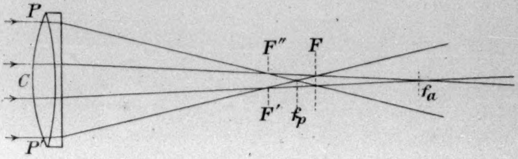


Fig. 2.

It will be seen that the images *a* and *b* are formed by light from opposite halves of the objective, and that the line of division of the latter is perpendicular to the direction of the displacement to be measured. The objection to this arrangement is twofold. In the first place, if the objective is not wholly free from spherical aberration, a spurious displacement in opposite directions is given to each image. Fig. 2 represents the case of a lens undercorrected for spherical aberration. If parallel light is incident on the whole lens the peripheral rays are brought to a focus at f_p, while rays near the axis converge to f_a. The circle of least confusion which represents the mean focus is situated at F, say, somewhere between f_p and f_a. If now light from the upper half, P C, of the lens be cut off, as is the case for the image from E F (Fig. 1), the circle of least confusion is no longer at F but at F′. Similarly, if C P′ be obscured as is the case for the image from A B (Fig. 1), the focus is at F″. Hence, even if the return beams leave A B and E F accurately parallel, the images *a* and *b* will be separated by an amount $F' F''$, which is only zero if the residual spherical errors are quite negligible.

In the second place, even with a perfectly corrected objective, the method depends for its success on the accurate focussing of the eyepiece on the images. In Fig. 3 let *a* and *b* be the true positions of the images from the two surfaces. If the focal plane of the eyepiece is a little behind or in advance of the true position, *a* and *b* will be seen as circles of confusion with centres situated at a' and b' or a'' and b'', as the case may be. In an actual case where the focal length of the object glass is large the sharpness of the images is sensibly uniform over an appreciable range. It is difficult to give a true indication of the magnitude of effects of this nature in a diagram in which dimensions are necessarily exaggerated, but the author has frequently found it to be possible, by racking the eyepiece out and in, to cause the images to move over a considerable range to and from each other without the definition being sensibly spoilt. It is, therefore, impossible to say that the correct displacement between *a* and *b* has been obtained.

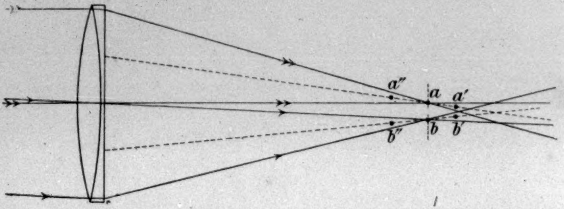


FIG. 3.

The unsatisfactory nature of all exact focussing methods was pointed out by Prof. Abbe, who showed that in many cases it could be surmounted by using "Telecentric" adjustment—an arrangement in which all parts of the image or images in the focal plane are formed by narrow pencils whose central rays are parallel to the axis. Unfortunately, telecentric adjustment is not possible in the type of measurement under discussion.

It is clear that the two sources of error mentioned above depend on the fact that the plane of division of the objective is perpendicular to the direction of the displacement which it is desired to measure, and the objections apply equally to any other method in which the objective is divided in this manner.

There are, however, certain cases in which matters can be arranged so as to avoid this difficulty. There are two methods open to us in the case already considered. If an optical flat is available, the standard block and the prism under test are placed side by side on the flat (Fig. 4), care being taken in each case to have the interference fringes running absolutely normal to the edges B B′ and E E′. The auto-collimator is then presented normally to the face A B′ and F E′, and the block (or prism) is gently tapped until the two images are in the same vertical plane. Their vertical displacement is then measured. In this case the plane of division of the objective is parallel to the plane of the measured displacement and neither spherical aberration nor depth of focus materially affects the displacement in this plane. Displacements due to these causes at right angles to the plane of measurement are, of course, immaterial, and are nullified in the preliminary adjustments. With this method, or any other involving the assumption of zero angle between two faces (such as those of the prism and block in Fig. 1, or each of those with the optical flat in Fig. 4), it is necessary to use considerable care in the adjustment of the fringes. A difference in the thickness of the air film corresponding to one interference fringe in a length of about 5 cm. is equivalent to 1 sec. of arc. The fact that there is parallax between the fringes and the film as the eye is moved about and the further difficulty of accurately interpreting their appearance when viewed through refracting surfaces, as has often to be done, renders it somewhat difficult to be sure that no error comparable with the degree of accuracy aimed at

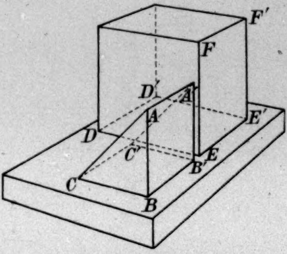


Fig. 4.

(1 sec. approximately in most of this work) remains from this adjustment.

A method which does not involve the adjustment of interference fringes is to mount the two angles which are to be compared, one above the other, as in Fig. 5. In the figure the prism is shown sitting on the side of the block, but it is, of course, essential to set it on a small levelling table which rests on the block in order that the edge B B′ may be adjusted to be parallel to E E′. This may be done by any of the ordinary methods. The collimator is then placed normal to the faces B A′ and E F′, so that the smaller one, B A′, is symmetrically placed from left to right when viewed through the telescope with eyepiece removed. The unsymmetrical portion of the face E F′ to the right of the dotted line is obscured by a suitable screen. When the adjustments have been properly made the images from B A′ and E F′ should be in a plane perpendicular to E E′. By measuring their displacement in this plane the small angle between the faces B A′ and E F′ is obtained. The base carrying the blocks is now cautiously rotated, so as to bring the images from C B′ and D E′ into the field of the collimator, the portion of D E′ to the left of the dotted line being screened off. As an alternative to rotating the base, the collimator may be moved round. The inclination of the faces C B′ and D E′ can now be obtained. From these two differences the value of the unknown right angle can be deduced. Although more laborious than the method of Fig. 4, inasmuch as the adjustment of the levelling screws is somewhat tedious and two measurements have to be made instead of one, this arrangement has been found to be preferable when the highest accuracy is desired.

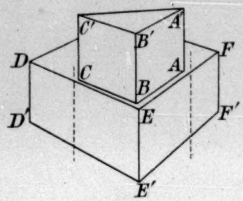
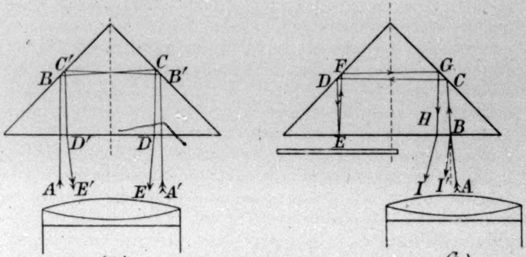


FIG. 5.

S. D. Chalmers and H. S. Ryland ("Transactions," Optical

Society, 1904-1905, p. 34) describe a number of attractive methods for determining the angles of prisms without standard comparison blocks. In two cases, however, the arrangements present the objectionable feature which has already been discussed. These are the cases of 90 deg. and 120 deg. In the first of these a parallel beam of light is incident approximately normally on the hypotenuse face (Fig. 6, *a*). The rays such as A, B, C, D, E incident to the left of the 90 deg. edge leave the prism in a direction D E, while the rays incident to the right of the edge come out in the direction D′ E′. The inclination of D E to D′ E′ depends only on the value of the right angle, and is measured by the auto-collimator. It will be seen that the two images in the field of the eyepiece are produced by light coming entirely from the right and left halves of the objective respectively, so that the uncertainties due to depth of focus and also to any spherical aberration which may exist are present. The method can readily be modified to avoid this disadvantage. One half of the prism is screened off (Fig. 6, *b*), and the auto-collimator is placed opposite the other half. When the necessary adjustments have been made the two images which will be seen in the field are produced by rays which have traversed the paths A, B, I′ and A, B, C, D, E, F, G, H, I respectively. The inclination of H I to B I′ depends, as in the previous case, on the value of the right angle only. In this case, however, corresponding rays in each image pass through the same portion of the object glass, and the small displacement of the



(a.) *(b.)*

FIG. 6.

images in the field of the eyepiece is unaffected by focussing or by spherical aberration.*

All the reflections except those at B and E are total, so that the images are of nearly equal intensity and quite bright enough for accurate measurements. The case of 120 deg. can be modified in the same way, but it is necessary in this case to silver the two faces containing the obtuse angle since the reflections at these faces are not total, and the image which undergoes multiple reflection would be too faint to observe.

This note may be concluded with a general observation on the relative merits of the auto-collimating methods and the more direct methods of measuring prism angles. The former are undoubtedly susceptible of greater accuracy where every possible precaution is taken to eliminate all sources of error such as those herein discussed. Nevertheless with a good quality circle reading to, say, 5 secs. by two or more micrometer microscopes, it is possible to determine prism angles correct to about 3 secs. or even less with reasonable care. While this accuracy may be exceeded if desired by auto-collimating methods, the necessary trouble which has to be taken in order to do so renders the process somewhat tedious.

With regard to a choice of method for determining angles in any given case it should be borne in mind that the maximum accuracy which it is useful to secure depends on the purpose for which it is intended to use the prism and the quality of the glass. For instance, in the case of a prism designed for measurements of refractive index, in which the deviation of narrow pencils passing through different portions of the material differ by as much as 10 secs., as is sometimes the case in prisms whose total performance is quite satisfactory, a knowledge of the angles to an accuracy greater than about 5 secs. is clearly superfluous, and the time spent in obtaining it is wasted.

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* It should be noted that this arrangement can only be used with convenience when the pyramidal error of the prism is small, *i.e.*, when the normal to the hypotenuse face is in or near the plane containing the normals to the other faces. It is clear that if this is not so the ray returning from E is deflected either downwards or upwards, while BI′ is deflected in the opposite direction. Hence the line of separation of the two images will not be in the plane containing the normals to the faces bounding the right angle. The component of the separation parallel to this plane will not, however, be affected, and it is this that should be measured. But it is difficult to obtain satisfactory measurements with most types of micrometer eyepiece if the line joining the two images is not nearly parallel to the traverse of the micrometer. The method is, therefore, only suitable for use in cases where this condition is fulfilled. Fortunately, among prisms of good quality the pyramidal errors encountered are rarely sufficient to cause trouble.

ABSTRACT.

The measurement of angles by means of the autocollimator resolves itself into the measurement of the distance between two images produced in the focal plane of a micrometer eyepiece. In most cases the light forming these images passes through portions of the object glass on opposite sides of a diameter. It is shown that, when this diameter is perpendicular to the direction of the displacement to be measured, uncertainty and error are introduced on account of any residual spherical aberration of the object glass and the depth of focus of the telescope. One or two particular cases are discussed in which it is shown how this may be obviated.

DISCUSSION.

Dr. R. S. WILLOWS asked why the Abbé type of autocollimating eyepiece, such as is used on Pulfrich refractometers, &c., was not employed in the arrangement described in the Paper.

The AUTHOR explained that there was a difficulty in adapting this method of illumination to a micrometer eyepiece.

XXIV. *The Viscosity of Colloidal Solutions.* By EMIL HATSCHEK.

RECEIVED MARCH 30, 1916.

IN his recent Guthrie Lecture on "Some Problems of Living Matter" ("Proc." XXVIII., Part II., p. 99), Mr. Hardy, in discussing gelation, makes the following remarks : "According to the theory of Einstein and Hatschek a decrease in fluidity is due to an increase in the volume of the colloid particles following upon an intake of water from the continuous medium. I do not think so simple a theory covers the facts. Their formula fails except in the case of the simplest hydrosols and suspensions."

This statement is based on, and may help to perpetuate, two misconceptions, which it seems desirable to clear up. In the first instance, no formula for the viscosity of a sol can by any possibility be applicable to a gel or even to the transition stage of gel formation. This is perfectly obvious, without any assumptions whatever on the structure of gels—a subject which is still highly debatable—if the remarkable elasticity of gels, to which Mr. Hardy refers, is remembered. As this elasticity is absent in the sol state, there must be a profound difference between the two systems, which at once precludes the possibility of representing their mechanical properties by the same formula.

In the second instance, Einstein's and my formula was never intended to apply to such systems as Mr. Hardy exclusively discusses, systems in which a transfer of water from the continuous into the disperse phase is possible. Although the methods used by Einstein * and by myself† in deducing the formula are entirely different, the assumptions regarding the constitution of the suspension are identical—viz., that the disperse phase consists of *rigid* spheres of such sizes as to conform to Stokes' formula—that these spheres in the aggregate occupy only a small portion of the total volume, and that they do not influence one another.

This definition—which is difficult to realise even in the case of true suspensions or suspensoids—can certainly not be held to apply at all to the class of colloids which form the contents of cells. The universal view is that these systems consist of two *liquid* phases, and the generic title "Emulsoids," which is very generally accepted for them, expresses this view. The disperse phase in such systems—*e.g.*, albumin, gelatin, silicic acid or rubber sols—is supposed to consist of deformable aggregate formed by the dispersed substance in association with a large and varying proportion of the dispersion medium.

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* A. Einstein, "Ann. d. Physik," XIX., 289, 1906.

† E. Hatschek, "Koll. Zeitschr." VII., 301, 1910.

For such sols, or generally for systems consisting of two liquid phases, I have given a formula which was published very soon after my suspensoid formula.* It applies to systems in which the disperse phase occupies the greater part of the total volume, so that its particles must assume a polyhedral shape. If such a system is sheared, deformation of the polyhedra must occur, the only force tending to restore them to their original shape being the interfacial tension between the two phases, which is necessarily small in any stable system. It is, therefore, probable that, at rates of shear exceeding a certain minimum, the structure remains deformed, so that the whole shear takes place in the thin films of continuous phase separating the polyhedra of disperse phase. The viscosity of the whole system can then be expressed by the following equation :

$$\eta' = \eta \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1} \quad \ldots \ldots \ldots \quad (1)$$

in which the symbols mean :—

A = the ratio total volume/volume of disperse phase.

η' = viscosity coefficient of system.

η = viscosity coefficient of continuous phase (dispersion medium).

It will be noticed that the value of η' increases very rapidly as A approaches unity—*i.e.*, as the disperse phase occupies more and more of the total volume; and this fact, as well as the shape of the curve defined by the equation, agrees perfectly with experimental data.

It will also be noticed that neither the *viscosity of the disperse phase* nor the *degree of dispersity* (the absolute size of the particles) appear in the equation. The absence of these factors, however, while surprising at first sight, is what renders the formula directly applicable to emulsoids, since both of them are unknown in these systems.

As regards A, the ratio total volume/volume of disperse phase, and experimental verification of the formula, which presumes that this value is known, a distinction must be made between emulsions proper—*i.e.*, dispersions of one liquid in another in which it is practically insoluble (*e.g.*, petroleum in dilute soap solution) and emulsoids sols.

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* E. Hatschek, "Koll. Zeitschr.," VIII., 34, 1911.

In the former the ratio A is known from the volumes used in preparation, or can easily be determined afterwards by breaking up the emulsion. The formula has been tested for such an emulsion, the viscosity being determined in a modified Couette apparatus at a low rate of shear.*. It will be seen that, by a simple transformation of the formula, the ratio A can be calculated from one viscosity determination. If, as is usually done, we make η the viscosity coefficient of the medium = unity we obtain :—

$$A=\left(\frac{\eta'}{\eta'-1}\right)^3, \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

from which A, and, therefore, the volume percentage of disperse phase ($100/A$) can be directly calculated. In the case of the petroleum-soap water emulsion the ratio found by direct determination was 79·8 per cent. of oil, while that calculated from the viscosity by applying equation (2) was 76·7 per cent., an agreement which must be considered quite satisfactory in view of the destruction which such emulsions undergo even at low rates of shear.

As regards the emulsoids, say, of sols of proteins, gum arabic or rubber, the case is somewhat different, since we cannot determine the volume of disperse phase directly. We can, however, again calculate it from a viscosity determination, and find that each gramme of dissolved substance, *at one particular concentration*, produces *n* cubic cm. of disperse phase. This single result naturally does not constitute any check on the formula, and to obtain one we must make some assumption as to the amount of dispersion medium associated with the dispersed substance at different concentrations. The simplest and most natural assumption is that the association factor is constant at least over a certain range. If this is true, we must obtain *a constant when dividing the volumes of disperse phase, as calculated from the viscosities of sols of various concentrations, by the amounts dissolved to obtain these concentrations.*

Such calculations have been carried out by myself † on published viscosity measurements of other observers, and by Miss H. Chick on viscosity measurements on the proteins of serum carried out by herself.* A very satisfactory constancy over a wide range was found in all cases. Thus, the relative viscosity of casein sol (water at the same temperature=1) rises from 6·12 at 6·05 per cent. to 23·72 at 9·39 per cent., while the association factors for these two extremes are 9·638 and 9·358. Miss Chick has also shown that the relative values of association for different proteins agree perfectly with their behaviour under various conditions involving an alteration in the amount of associated water—*e.g.*, in salting out—at higher temperatures, &c.

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* E. Hatschek, "Colloids and their Viscosity," "Trans." Faraday Soc., LVII., 1913.

† *Loc. cit.*, IV., p. 56.

It is possible to obtain evidence of the correctness of the formula, or at least of the views on which it is based, in another manner. Some colloids, like rubber, which can be dissolved in a number of different solvents, show very different viscosities in them at equal concentrations. If the views here discussed are correct this should mean that rubber is associated with a large volume of the dispersion medium when showing high viscosity and with a small volume in the sols exhibiting low viscosity. Now, it is known that rubber swells considerably, but to a very different extent, in the liquids in which it ultimately dissolves. It is only reasonable to assume that the amounts of associated solvent calculated from the viscosity, and the amounts absorbed in the preliminary swelling, should show some agreement. An investigation in this sense has been carried out by Kirchhof.† He determined the viscosity of rubber sols in different solvents, and calculated from them the amount of associated solvent according to formula (2). A comparison of the figures so obtained with the figures for solvent taken up in preliminary swelling—published by another observer, Posnjak—shows "remarkable agreement," not only in their relative order, but even in absolute amount.

To sum up—

1. No conceivable viscosity formula can cover the stage of gelation.
2. The suspensoid formula deduced by Einstein and independently by myself applies only (and imperfectly) to systems in which the disperse phase consists of rigid spherical particles.

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* H. Chick, "Biochem. Journal," VIII., 261, 1914.

† F. Kirchhof, "Koll. Zeitschr.," XV., 30, 1914.

3. A formula for emulsoids—*i.e.*, systems in which the disperse phase is also liquid—published in 1911, has since received a considerable amount of experimental confirmation.

ABSTRACT.

The author, in reply to some remarks made by Mr W. B. Hardy in the course of his Guthrie lecture, points out (*a*) that no viscosity formula can cover the stage of gel formation, since the change from a liquid with only slight anomalies to a system having many properties of an elastic solid necessarily precludes this, and (*b*) that the formula given by Einstein, and independently by himself, for the viscosity of a suspension of rigid spherical particles, does not in any event apply to systems such as discussed by Mr. Hardy, which belong to the class known as emulsoids. In these both phases are quite generally assumed to be liquid, and an expression for the viscosity of such systems was deduced by the author in 1911, from a consideration of the deformation which a homogeneous polyhedral structure must undergo when sheared. The expression contains only the viscosity of the system and the phase ratio, but neither the interfacial tension of the phases nor the viscosity of the disperse phase. It can be tested directly for emulsions of two immiscible liquids; in the case of emulsoids, where only the weight of dispersed substance is known, some assumption has to be made about the relation between the volume of disperse phase formed—*i.e.*, the degree of hydration or solvation—and the weight dissolved. The simplest assumption, that this ratio is constant, has been tested by the author, and by Dr. Harriette Chick, for a number of sols, and is found to hold good over a considerable range. The formula has also been tested by F. Kirchhof in a different way, by comparing the degree of solvation—*i.e.*, the amount of solvent taken up by the disperse phase in different solvents—with the amount of the solvent taken up by the substance (indiarubber) in the swelling which precedes dispersion. Remarkable agreement both in the order and in the absolute amounts in different solvents was observed.

DISCUSSION.

Dr. A. GRIFFITHS said he was in emphatic agreement with the conclusion at the end of paragraph two. He mentioned the case of a gelatine which would not run through a capillary tube, but which could be made to do so when broken up by stirring with a stick. He thought experiments on rigidity as well as viscosity should be made.

The AUTHOR, in reply to a remark by the President, stated that accidental double refraction was sometimes observed in the liquid phase.

XXV. *A Recalculation of Some Work on Diffusion by Dr. A. Griffiths and Others.* *By* A. GRIFFITHS, *D.Sc.*

RECEIVED APRIL 24, 1916.

THE Papers which require certain corrections are :—

I. "Determination of the Coefficient of Diffusion of Potassium Chloride by an Analytical Method." By A. Griffiths, J. M. Dickson and C. H. Griffiths, "Proc." Phys. Soc., Vol. XXVIII., Part I., Dec. 15, 1915.

II. "On the Coefficient of Diffusion in Dilute Solutions." By B. W. Clack. "Proc." Phys. Soc., Vol. XXVII., Part I., Dec. 15, 1914.

III. "On the Temperature Coefficient of Diffusion." By B. W. Clack. "Proc." Phys. Soc., Vol. XXIV., Part I., Dec. 15, 1911.

IV. "On the Coefficient of Diffusion." By B. W. Clack. "Proc." Phys. Soc., Vol. XXI. May, 1909.

In the experiments described on the above Papers diffusion takes place along a vertical tube, or a series of vertical tubes.

The lower ends of the tubes are kept in contact with a solution at a constant concentration, and the upper ends are generally kept in contact with water. It is shown that the liquid in the tubes is in movement, and reference is made to the velocity of the liquid through which diffusion takes place ; but what is meant by the velocity of the liquid is unfortunately not explained ; and it would have been better to deal with the *velocity of the water component of the liquid*, to which a clear meaning can be attached.

The majority of the symbols given on page 73 of the first Paper on the list retain their specifications, but the meaning of V should be taken to represent the velocity of the water-component of the solution, and not the velocity of the liquid.

With the new meaning of V, equations (1) and (2) on page 73 still hold good ; but equation (4) on page 74 is incorrect ; for c represents the total mass of potassium chloride proceeding from the reservoir per unit area per second, and its place is taken by water and by water only.

Thus $V\times$mass of water in one continuous current of solution at end of tube$=c\delta$.

$$\therefore\ V(D-N)=c\delta$$

and

$$v=c\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (5) is now redundant.

Equation (3), p. 74, should have been.

$$\frac{N-n_0}{c}\left\{1-\frac{v(N+n_0)}{2c}\right\}=\frac{L}{K}.$$

Finally, equation (6), p. 74, takes the form

$$K=\frac{Lc}{(N-n_0)}\;\frac{1}{1-\frac{1}{2}(N+n_0)\delta}.$$

It may be mentioned incidentally that when the tops of the tubes are in contact with water the corrected equation (4) may be obtained by noting that the volume-movement of the water downwards at the upper ends of the tubes must be equal to the diminution in volume of the solution in the reservoir due to the escape of the potassium chloride.

The value of K given in the first Paper must be multiplied by

$$\frac{1-\frac{1}{2}(D-N)(N-n_0)\delta}{1-\frac{1}{2}(N+n_0)\delta}.$$

The correcting value varies from 1·005 to 1·01, and has a mean value of 1·007. Thus the corrected value of K_{18} in the case of a solution of potassium chloride containing 0·2237 gramme to the cubic centimetre (a 3N solution) is 1·696; and the corrected value of $K_{18\cdot5}$ is 1·715.

In the last Paper on the list at the head of this note, equations (1), (2) and (3) are unaffected; but equation (4) becomes

$$K=\frac{Li}{N\left(1-\frac{N\delta}{2}\right)(1-\delta)}.$$

Thus the values for K in all Mr. Clack's Papers must generally be multiplied by

$$\frac{\left\{1-\frac{N\delta}{2}(D-N)\right\}\;\{1-\delta(D-N)\}}{\left(1-\frac{N\delta}{2}\right)(1-\delta)}.$$

Mr. Clack will correct the whole of his summarised results himself; but I have his permission to deal with the case of a 2·7 normal solution of potassium chloride. In the case of feeble solutions the multiplier approaches unity, but in the case under consideration its value is 1·062.

Thus his corrected value of K_{18} is $1{\cdot}628 \times 10^{-5}$; and the corrected value given by Paper I. is only 4 per cent. greater than that obtained by Mr. Clack.

I may be allowed to remark that the value of K_{18} deduced from my Paper on Diffusive Convection, in the "Proc." Phys. Soc., Vol. XXVIII., Part I., December, 1915 (to which fortunately no correction is necessary), is $1{\cdot}617 \times 10^{-5}$. This is only 0·7 per cent. less than Mr. Clack's corrected value.

There is no doubt that, as thus recalculated, the results given by the three methods agree within the limits of experimental error; and my opinion is that the true value of the coefficient of diffusion lies close to those given by Mr. Clack's gravitational method, and by my convective method.

XXVI.—*On a Method of Measuring the Pressure of Light by Means of Thin Metal Foil. Part II.*

By GILBERT D. WEST, *B.Sc.*

RECEIVED MAY 12, 1916.

IN an earlier Paper to the Physical Society* I have described the measurement of the pressure of light by a method requiring few of the elaborate precautions generally necessary in such experiments. The essential feature of the apparatus was a strip of gold leaf suspended in the middle of a test tube containing air or hydrogen at reduced pressure. Radiation from a 32 c.p. carbon filament lamp, impinging directly on one side of the strip, was sufficient to cause a microscopically measurable deflection of the end.

The pressure of normally incident radiation on a perfectly reflecting surface has been shown† to be numerically equal to twice the energy content of the radiation per unit volume, and hence if this quantity be measured in the way described below, a check on the original observations can be made. A mean of the results of several successive experiments with the deflected strips, gave a value for the pressure of radiation which only differed from that calculated from the energy density by a small per cent. The accuracy and constancy of the final results seemed to preclude their being seriously affected by gas action, but as gas action had to be taken into consideration, the present research was undertaken with a view to its fuller investigation, and if possible to its complete elimination.

As it is convenient to know in advance the value of the true pressure of the radiation employed, the measurements and calculations required for this purpose will be dealt with first.

Measurement of the Energy Density.

The method used was similar to that described in the previous Paper. The initial rate of rise of temperature of a blackened copper plate enclosed in the tube, was measured by means of an attached copper eureka thermo-junction. Due allowance was made for cooling corrections, and the lamp black was again assumed to absorb 95 per cent. of the incident radiation. The cold junction was immersed in oil contained in a vacuum flask, and during an experiment a delicate indicating thermometer in the oil, only showed negligible variations. The calibration of the thermo-junction was carried out in the usual way, and a number of minor matters received fuller consideration than was previously given.

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* "Proc. Phys. Soc.," Vol. XXV., 1913, p. 324.

† Maxwell, "Electricity and Magnetism," Vol. II. Larmor, "Encycl. Brit.: Radiation." *See also* Callendar, "Nature," Jan. 1, 1914.

When, from the measurements thus taken, the energy reaching 1 sq. cm. in one second is known, the energy per 1 c.c. can be calculated from a knowledge of the velocity of light.

The 32 c.p. lamp was enclosed in a metal box whose front face had been replaced by a glass screen covered with a few thin wires. Inasmuch as it is required that the radiation should be normally incident, the lamp was not brought too close to the tube—a calculation of the limiting approach having been previously made. The current passing through the lamp was kept at the same value throughout all the experiments.

The results obtained are indicated in the course of the ensuing work. Owing to extraneous thermo-electric effects, especially at brass contact screws*, the accuracy was not quite as great as had been hoped. Nevertheless on drawing a curve evenly between the points representing the energy density at various distances from the source, it was found that none of the readings diverged by more than about 3 per cent. This accuracy is above what is required.

Reflecting and Transmitting Powers of the Foils Used.

By coating the front surface of the copper plate of the apparatus described in the previous Paper, with the foil to be used instead of with lamp black, it was possible to obtain measurements of the fraction of the incident radiation that was absorbed. More satisfactory results, however, were obtained with an apparatus somewhat similar to that originally used by Lebedew.† The bulb of a sensitive thermometer was fitted into a hole in a small block of copper. Thermal contact was secured by means of a little mercury, and the whole was placed in the tube in which subsequent measurements were carried out. The front face of the block was first coated with lamp black and afterwards with the foil under observation, whilst the rates of rise of temperature on exposure to radiation, were, in each case, measured by means of a magnifying cathetometer telescope.

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* A. G. Warren and F. Murphy, "Electrician," Jan. 31, 1908.

† Lebedew, "Ann. der Physik," VI., p. 433, 1901.

By interposing a screen made of gold or aluminium foil, between the source and the blackened block, it was possible to show that neither kind of foil transmitted an appreciable fraction of the incident radiation. The only correction therefore in calculating the reflecting power of the foil, is the re-reflection* from the glass of the tube. This amounts to about 7 per cent. Re-reflections after the first need not be considered.

As a mean of several observations, it was found that both gold and aluminium foil reflected 90 per cent. of the incident radiation.

It was also found that light was reflected from a sheet of foil, in a direction sufficiently close to the normal for the purposes of the experiment.

Calculation of the Deflection of the Strip.

Since the foil reflects 90 per cent. of the incident radiation, and since 7 per cent. is re-reflected from the glass of the tube, the total pressure of the radiation is given by

$$E(1+0{\cdot}07\times 0{\cdot}9)(1+0{\cdot}9) \text{ or } 2{\cdot}04E$$

where E is the energy density of the incident beam.

A certain amount of radiation, however, strikes the back of the glass tube, and some of this is reflected to the back of the strip. For a strip three-quarters the width of the tube, it is estimated that the normal component of this radiation is about 1 per cent. of all that is incident on the strip. It is therefore necessary to substitute $2{\cdot}02E$ for $2{\cdot}04E$.

It can be shown that a uniform flexible strip when deflected by a small uniform pressure, still remains straight. To a close degree of approximation, therefore, we may calculate the deflection of a strip such as that represented in Fig. 1, by taking moments about the axis of rotation.

It was considered preferable in this research to find, by means of a Bunge balance, the mass of 1 sq. cm. of the sheet of foil from which the strip was cut, rather than to weigh the strip itself, and we may modify the original formula accordingly.

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* Re-reflection was not considered in the original Paper. I have to thank the late Prof. Poynting and Dr. Barlow for the suggestion.

If we write h the distance of the centre of gravity of the strip below the axis of rotation AB as $\frac{l^2+f^2}{2(l+f)}$, where f is the length of the folded part AC, Fig. 1. We may write the deflection of the end of the strip of length l as

$$d=\frac{2{\cdot}02El}{\left(1+\frac{f^2}{l^2}\right)\rho g}.$$

where ρ is the mass of 1 sq. cm. of the foil.

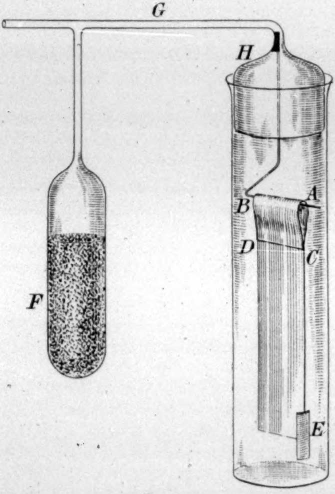

Fig. 1.

The Apparatus.

There are a few modifications of the original apparatus that need explanation. The top of the tube was closed by the hollow stopper H. In order to obtain a clear image of the end of the strip a small piece of cover glass was cemented to the inside of the tube at E by means of solid Canada Balsam. Another piece of cover glass was attached to the outside of the

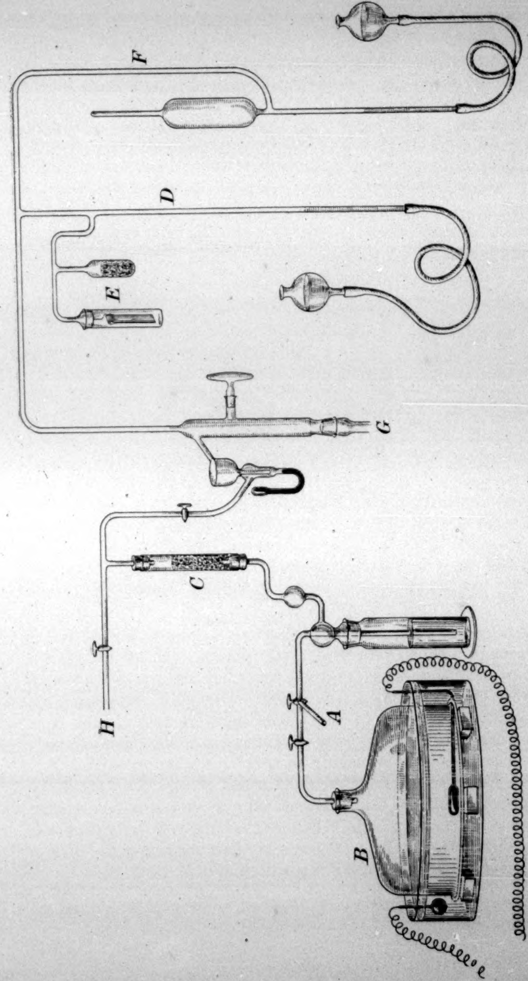

Fig. 2.

tube with a viscous solution of Canada Balsam in Xylol. By this means it was found possible to get improved definition of the image given by the microscope. When it was required to obtain very high vacua, a tube was attached similar to *F*, containing charcoal that had been prepared by very slowly calcining elder pith.* In the ordinary course of events, however, the tube *G* was connected directly to a motor-driven Gaede pump and a McLeod gauge.

The general arrangement of the apparatus is shown in Fig. 2. Air may be admitted to the pump at *A*, but by a turn of the cock, electrolytically generated hydrogen from the reservoir *B* may be admitted instead. Before entering the pump, the gas is forced to pass, first through strong sulphuric acid and then through a tube *C* containing phosphorous pentoxide. *D* is a barometric seal which prevents any small leakage to the tube *E* when the pump has ceased action. *F* is a McLeod gauge, *G* is directly connected to the Gaede mercury pump, and *H* is connected to a rotary pump exhausting to about 1 cm. mercury.

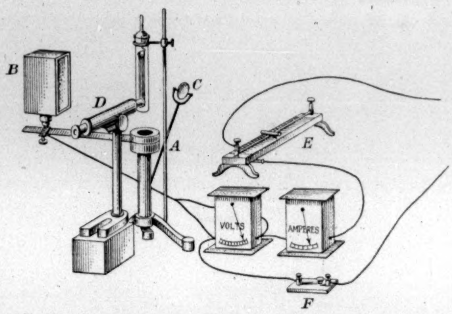

FIG. 3.

The apparatus for taking observations is represented in Fig. 3. The tube is mounted on a stand *A*, specially made by Messrs. Griffin & Co., and the lamp *B* can easily be swung round from side to side. Behind the tube is a small mirror *C* to illuminate the field of vision of the microscope *D*. *E* is a variable resistance, and *F* is a switch.

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* In this connection I have to thank Dr. S. W. J. Smith for valuable suggestions.

A No. 3 Leitz objective coupled with a X20 eyepiece was used in the observing microscope. The slight chromatic aberration was reduced by means of a yellow screen placed in front of the eyepiece.* Before exhausting the tube, the stopper was sealed down with a mixture of wax and resin. The pump was probably capable of evacuating to pressures considerably below the vapour pressure of mercury,† but as no special precautions were taken, this was not generally attempted. For very low vacua, reliance was placed on liquid air and charcoal.

RESULTS.

Expansion of the Strips, due to Rise of Temperature.

Much light is thrown on the main issues, by a subsidiary phenomenon which escaped notice in the original Paper, owing probably to the bad definition of the image in the microscope, caused by the glass of the test tube.

The phenomenon referred to is the expansion of the strip under the influence of the radiation. To observe the expansions it was necessary to attach pieces of copper foil to the ends of the strips, as otherwise the movements under the influence of radiation prevented accurate observation. The expansion takes place rapidly, and is small and constant for gas pressures down to 1·5 cm. Below this it shows a slight increase, and then remains constant until a pressure of about 0·002 cm. is reached. On lowering the pressure still more it increases, until with the lowest vacua obtainable, it is nearly 20 times the original value. A series of results is given below.

ALUMINIUM STRIP.

Length = 7·43 cm. Distance of lamp = 10·5 cm. Energy density of radiation $= 1{\cdot}95 \times 10^{-5}$ ergs./cc.

Pressure.	Expansion of strip in air.
74·3 cm. of mercury (atmosphere)	$0{\cdot}5 \times 10^{-3}$ cm.
41·3 cm.	0·5 ,, ,,
24·3 cm.	0·5 ,, ,,
5·0 cm.	0·5 ,, ,,
1·5 cm.	0·5 ,, ,,
0·35 cm.	0·6 ,, ,,
0·027 cm.	0·6 ,, ,,
0·0025 cm.	0·8 ,, ,,
0·0005 cm.	1·6 ,, ,,
0·0001 cm.	2·4 ,, ,,
Liquid air vacuum.	8·7 ,, ,,

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* I am indebted to Dr. Salisbury, of East London College, for this suggestion.

† "Gaede Sci. Abs.," p. 471, 1915; also "Ann. der Physik," 46, p. 357, 1915.

When the apparatus was filled with hydrogen (whose thermal conductivity is six times that of air), the expansions for pressures down to 0·005 cm. were scarcely observable, being about $0{\cdot}1\times10^{-3}$ cm. They increased after that point however.

The rises of temperature that the expansions of the strips imply, are shown in the table below. The values assumed for the co-efficients of expansion of aluminium and gold are $25{\cdot}5\times10^{-6}$, and $13{\cdot}9\times10^{-6}$, respectively.*

Pressures.	Rise of temperature (Degrees Centigrade).			
	Aluminium strip.		Gold strip.	
	In air.	In hydrogen.	In air.	In hydrogen.
74·3 cm.	2·5	Hardly observable, about 0·5	1·8	Too small to be observed
Liquid air vacuum	46·0	...	44·5	...

The estimated difference of temperature of the two sides of the aluminium and gold strips respectively, was 6×10^{-7}°C., and 9×10^{-8}°C. No effects attributable to these small differences of temperature have yet been observed.

The results are almost self explanatory. Convection, conduction and radiation each play a part in determining the temperature of the strip at pressures down to about 1 cm. Conduction is independent of pressure unless this is very low, and, together with radiation, is the important factor until the very lowest pressures are reached, at which radiation alone is important. Thus at high pressures the rise of temperature is small, but at very low pressures it is considerable. The results obtained are in general agreement with those of Kundt and Warburg,† and they are in close agreement with the more precise results of Sir William Crookes.‡

The accepted view that convection is unimportant at pressures below 1 cm. is confirmed, and in the work shortly to be described, it will be found that satisfactory explanations of phenomena can be given by neglecting convection, at low pressures, altogether.

The Thermo-Kinetic Reaction.

The motion of the strip under the influence of radiation was considered in the previous Paper down to a pressure of about

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* Voigt, 1893.

† "Pogg. Ann.," CLVI., p. 177, 1875; also "Phil. Mag.," July, 1875.

‡ "Proc. Royal Soc.," Vol. XXXI., p. 239, 1880-81.

1 cm. At that pressure, only very small gas action effects make their appearance, but as the pressure is lowered to, say, 0·002 cm., the movements of the strip may become a hundred times as large as before.

The strip may move initially either towards or from the source, and the first movement is followed by a much slower movement which is always away from the source. The first movement is strongest when the tube is inclined to the vertical —that is to say, when the end of the strip is nearer to one side of the tube than to the other. A typical series of readings for various pressures is given below in the table and in the diagrams on following page. It will be noted that in spite of the inclination of the tube, reasonable values for the pressure of light are obtained both at 1·5 cm. and 0·9 cm. of mercury.

ALUMINIUM STRIP.

Length = 7·43 cm. Distance of lamp = 10·5 cm. Energy density of radiation = $1{\cdot}95 \times 10^{-5}$ ergs./c.c. Tube inclined so that end of strip was nearer to right side of tube. Observations taken at the end of the first movement.

Pressure.	Deflections.		Mean deflection from lamp.	Deflection calculated from energy density.
	Lamp on left side.	Lamp on right side.		
1·5 cm. Hg.	$0{\cdot}3 \times 10^{-3}$ cm. towards lamp	$6{\cdot}6 \times 10^{-3}$ cm. from lamp	$3{\cdot}1 \times 10^{-3}$ cm.	$2{\cdot}6 \times 10^{-3}$ cm.
0·9 cm. Hg.	1·6	7·9	3·1	2·6

When the tube was inclined in the opposite way, so that the end of the strip was nearer to the left side than to the right, a similar series of curves, as given on following page, was obtained, but the initial deflections were to the right instead of to the left. When the tube was filled with hydrogen, and when the aluminium leaf was exchanged for one of gold, similar curves were again obtained. The material of the strip and the nature of the gas seemed to have little influence on the results.

As shown by the curves the slow progressive movement that occurs when the first movement is over, is always away from the source, and it is therefore natural to attribute this motion to the gradual warming up of the surface of the tube. Further, it is possible to reduce greatly the ratio of the rate of this motion to the deflection, by the interposition of a thick glass plate in the path of the radiation. At low pressures, when the mean free path is a few centimetres, we may consider the strip to be bombarded by molecules returning from the heated glass surface. The strip is therefore deflected in the way observed. As the surface of the glass still remains hot when the lamp is switched off, and as the bombardment therefore continues, the strip does not return to zero for some time.

As was observed in the expansion experiments, the heating of the strip takes place rapidly, and it is this heating of the strip that accounts for the first part of the curves.

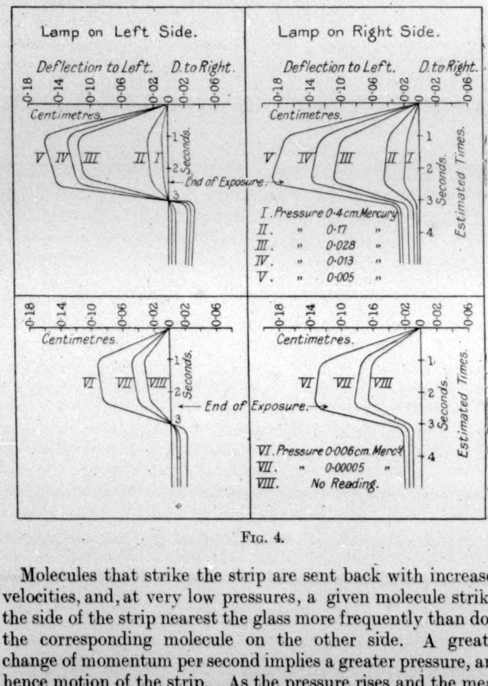

FIG. 4.

Molecules that strike the strip are sent back with increased velocities, and, at very low pressures, a given molecule strikes the side of the strip nearest the glass more frequently than does the corresponding molecule on the other side. A greater change of momentum per second implies a greater pressure, and hence motion of the strip. As the pressure rises and the mean free path is reduced, molecular collisions complicate the problem, and the simple theory needs the same elaborate modification that was given by Prof. Osborne-Reynolds* in connection with the theory of the Crookes Radiometer.

The deflections of the strips due to the heated glass rendered the apparatus unsuitable for the observation of the pressure at which the gas action effect described above reached a maximum, and recourse was therefore had to the weighted gold and aluminium strips used in the expansion experiments. It was found that throughout the region of pressures 0·01 cm. – 0·0005 cm. there were no great variations. The maximum in hydrogen was much the same as in air. To be certain of any difference, more precise experiments would be required. The results are similar to those of Sir William Crookes,† although the conditions are somewhat different. A comparison is given in the table below.

GOLD STRIP.

Pressure.	Deflections obtained.	Magnitude of radiometer effect calculated from Crookes' results.
0·16 cm. mercury	0·1 eyepiece divisions	1·0
0·02 ,,	0·4 ,, ,,	3·9
0·002 ,,	0·55 ,, ,,	8·3
0·0005 ,,	0·50 ,, ,,	4·1
0·0001 ,,	0·40 ,, ,,	2·0
0·00005(?) ,,	0·35 ,, ,,	1·7

To confirm the above theory a strip was mounted in a small rectangular glass cell in such a way that by tapping the cell the strip could be moved from side to side. The apparatus is represented in Fig. 5. The radiation may be allowed to fall normally on either side of the strip, but the deflection is always away from the closest glass surface, and is easily visible to the naked eye when the strip is placed so as to be nearly in contact with the glass. When the strip is in the middle of the containing vessel no movements are apparent.

The excess of pressure above the normal gas pressure that a heated surface experiences has been termed the thermo-kinetic reaction.

In the Crookes Radiometer the motion of the vane is caused by the difference of the thermo-kinetic reactions, due to the difference of the temperatures of the two sides of the vane.

In the Radiometer described above the initial motion of the strip is caused by the difference of the thermo-kinetic reactions on the two sides of the strip, arising from their different distances from the walls of the containing vessel.

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* "Phil. Trans.," II., 1879, p. 768.

† "Phil. Trans.," I., 1879, p. 133.

Under certain conditions, more complicated movements of the strip may occur. As it is proposed, however, to deal more fully with the subject in a subsequent Paper, further space will not be devoted to it here.

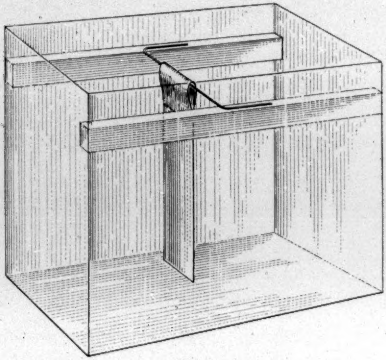

FIG. 5.

The Pressure of Radiation.

Under the new conditions, it is evident that to obtain trustworthy values of the pressure of radiation :—

(i.) The strip should be as central as possible.
(ii.) The vacuum should be very high.

The latter object was attained by the use of liquid air and charcoal. Further, only short exposures of about one second, were given, and the source of radiation was placed first on one side and then on the other. Any small deflection due to the difference of thermo-kinetic reaction on the two sides of the strip would therefore be eliminated by taking half the sum of the two readings.

The viscosity of a gas remains constant over wide ranges of pressure, but at very low pressures it is much reduced.[*] As a result, it was noticed that with liquid air vacua the strip was kept constantly vibrating like a pendulum by accidental tremors. The period of vibration was 0·45 sec., a value which agrees with the period of vibration of a flexible chain of the same length. A great advantage of the original apparatus, namely, its comparative insensitiveness to vibration, was thus lost at very low pressures. By mounting the apparatus, however, on the concrete floor of a basement, and by waiting for quiet intervals, some reasonably good results were obtained for the pressure of radiation. A series of results taken in succession is given below.

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[*] Crookes, "Phil. Trans.," 172, Part II., p. 378.

GOLD STRIP.

Liquid air vacuum. Energy density of radiation when lamp 10·5 cm. distant $=1{\cdot}95\times10^{-5}$ ergs /c.c. Length of strip $=7{\cdot}10$ cm. Length of folded part AC $=1{\cdot}02$ Mass of 1 sq. cm. of gold leaf $=1{\cdot}82\times10^{-4}$ gm.

Distance of source.	Deflections from lamp.			Deflections calculated from energy density.
	Lamp on left side.	Lamp on right side.	Mean.	
10·5 cm.	$2{\cdot}5\times10^{-3}$ cm.	$3{\cdot}2\times10^{-3}$ cm.	$2{\cdot}8\times10^{-3}$ cm.	$1{\cdot}6\times10^{-3}$ cm.
11·5 cm.	1·9	2·7	2·3	1·4
12·5 cm.	1·7	2·2	2·0	1·2

The reason why all the preceding results are too high has not been explained, and it is proposed to undertake further investigations on the matter. Other results obtained with the gold strip were also too high, but better results were obtained with the aluminium strip. They are recorded below.

ALUMINIUM STRIP.

Liquid air vacuum. Energy density of radiation when lamp is 10·5 cm. distant $=1{\cdot}95\times10^{-5}$ ergs./c.c. Length of strip $=7{\cdot}43$ cm. Length of folded part AC $=0{\cdot}83$ cm. Mass of 1 sq. cm. of aluminium foil $=1{\cdot}16\times10^{-4}$ gm.

Distance of source.	Deflections from lamp.			Deflections calculated from energy density.
	Lamp on left side.	Lamp on right side.	Mean.	
10·5 cm.	$2{\cdot}4\times10^{-3}$ cm.	$2{\cdot}5\times10^{-3}$ cm.	$2{\cdot}5\times10^{-3}$ cm.	$2{\cdot}6\times10^{-3}$ cm.
11·5 cm.	2·0	2·1	2·0	2·3
12·5 cm.	1·6	1·3	1·5	2·0

Other results obtained with the aluminium strip were similar to those above.

By inclining the tube it was found possible to increase the difference of the thermo-kinetic reactions on the two sides of the strip, but this effect was always comparatively small.

The results are similar to those obtained in the previous research. Moreover the disturbing effects which were then attributed to convection, were really effects of the same kind as those described in this Paper.

Starting at atmospheric pressure, the thermo-kinetic reaction increases as the pressure is diminished, until a maximum is reached at a pressure of about 0·002 cm. of mercury. Experiments on the pressure of light may be advantageously carried out as far below the maximum as possible, or as far above the maximum as convection currents will permit. The latter alternative is the easier, and appears to give more consistent results.

In conclusion, I have pleasure in thanking Prof. Lees for valuable suggestions, and for affording me every facility for prosecuting this research.

ABSTRACT.

The pressure of the radiation emitted by a carbon filament lamp at a distance of a few centimetres, is sufficient to cause a microscopically measurable deflection of the end of a strip of gold or aluminium foil, suspended in a closed test tube. By this means the radiation pressure may be measured, and the results may be checked by a comparison with the energy density of the radiation, as deduced from the initial rate of rise of temperature of an exposed blackened copper plate.

In a previous Paper, experiments were carried out in atmospheres of air and hydrogen, and at pressures extending from 76 cm. to 1 cm. of mercury. Under certain conditions it was found possible to obtain satisfactory results. The present Paper deals with experiments at pressures from 1 cm. of mercury down to the highest exhaustions that could be reached.

As the pressure is lowered, certain gas-action effects make their appearance, but, inasmuch as there is no appreciable difference of temperature on the two sides of the strip, the effects are somewhat different from those that occur in the ordinary type of Crookes' radiometer.

When the surface of the strip is closer to one side of the containing vessel than to the opposite side, a deflection away from the closer side occurs, and the direction of this deflection is independent of the side of the strip on which the radiation falls. With a symmetrically-placed strip the deflection should be negligibly small. An explanation of these effects is suggested in the Paper, and a special type of radiometer is described.

The nature of the residual gas in the tube does not seem to be very important, but it is found that the repulsive force acting on the strip increases with decreasing pressure, until a maximum is reached at about 0·002 cm. of mercury. With further reduction of pressure a progressive decrease takes place.

By symmetrical suspension, and by the use of liquid air and charcoal, it is possible so to reduce the gas action effect that measurements of the pressure of light of reasonable accuracy are again possible.

Experiments on the pressure of light may thus be advantageously carried out at the highest vacua obtainable, or at pressures as far above 0·002 cm. of mercury as convection currents will permit. The latter alternative is the easier, and leads to more consistent results.

DISCUSSION.

Mr. D. Owen (communicated remarks) thought the author was to be congratulated on his determined attempt to eliminate gas action at the lowest possible vacua. It appeared, from the tables at the end of the Paper, that even at the lowest pressures the deflection of the leaf differed according to the direction of the incident light. Such dissymmetry as is thus implied in the apparatus might also account for the different effects obtained with gold and aluminium. Observations with much larger vessels appeared to be desirable. The optical arrangements might perhaps be modified to avoid the contiguity of the leaf to the microscope objective. Such conditions might also be expected to enhance the undoubted advantage of the author's method, namely, rapid attainment of the final state; in some of Poynting & Barlow's experiments as much as an hour was found necessary. Had the author found it practicable to calculate the gas pressures, at the highest exhaustions, from the damping of the foil?

The Author, in reply, stated that he was in agreement with Mr. Owen as to the desirability of using larger containing vessels. It was felt, however, that before attempting more accurate measurements, a fuller investigation of the gas action was necessary. Owing to the disturbing effect of incessant tremors it had not yet been found possible to obtain an estimate of the pressures at the highest exhaustions, by observing the degree of damping. A modification of the method of mounting the strips might make such observations possible.

XXVII. *The Viscosity of Suspensions of Rigid Particles at Different Rates of Shear.* *By* EDITH HUMPHREY, *B.Sc., Ph.D., and* EMIL HATSCHEK.

RECEIVED MAY 12, 1916.

THE present investigation was undertaken with the object of discovering the relation between the concentration, the rate of shear and the viscosity of a suspension of rigid particles in a liquid. As students of the colloid state know, the viscosity of colloidal solutions gives one of the criteria by which such solutions are divided into two classes : One class (*e.g.*, colloidal solutions of metals or metallic sulphides) shows viscosities very little in excess of that of the solvents ; the other (*e.g.*, colloidal solutions of hydroxides, proteins, &c.) exhibits marked increase in viscosity. Rubber and nitrocellulose are extreme cases of this latter class, as solutions of less than 1 per cent. have viscosities 20 to 100 times that of the solvent. It has been generally accepted that these differences of behaviour may be explained as due to a difference in the form of the particles, or, as it is called, of the disperse phase. A suspension of solid, or, more properly, rigid, particles gives a low increase of viscosity, and the corresponding colloids are known as suspensoids ; on the other hand, the great increase in viscosity is accounted for by the presence of liquid (or deformable) particles in emulsions or emulsoid sols.

The mathematical treatment of a suspension of rigid particles in a liquid must, of course, be confined to spheres of such size as to follow Stokes' law, but within these limits is quite simple.* Only the principle of the treatment need be given here : A layer of liquid containing in suspension small rigid spheres is being sheared between two parallel plates, one of which is stationary, while the other travels in its own plane. It is obvious that the transverse velocity of the liquid at the upper pole of any sphere will be greater than that at the lower pole, so that the spheres may be considered to have a translatory motion relative to the liquid, the velocity of which is equal to half the difference of the velocities at the two poles. The extra work done in moving the particles can be calculated on Stokes' formula, assuming that the particles do not interfere with one another—that is to say, that there is no turbulence.

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* E. Hatschek, "Kolloid-Zeitschrift," VII., 301 (1910).

This work on the particles is done in addition to that expended in shearing the liquid, and may be added to it, the sum being the work required to shear the whole suspension, and thus the viscosity may be reduced, and is found to be

$$\eta_c = \eta_0(1 + 4{\cdot}5f),$$

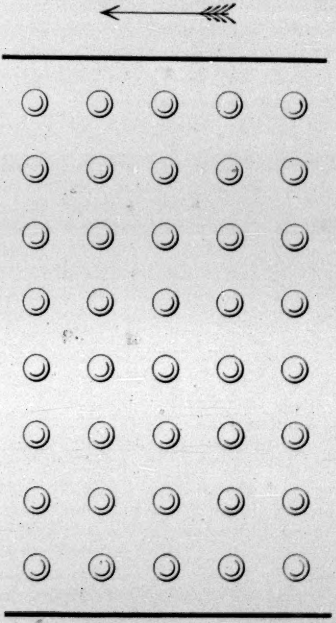

FIG. 1.

when

η_c = viscosity coefficient of the suspension of concentration C.
η_0 = viscosity coefficient of the liquid.
f = the ratio $\dfrac{\text{aggregate volume of solid particles}}{\text{total volume of suspension}}$.

Since the radius of the particles does not appear in the formula the viscosity should be independent of the latter (a result which is somewhat surprising), and the increase in viscosity caused by the suspended particles should be simply proportional to the aggregate volume.

A similar result had been obtained by Einstein in 1906.[*] He deduced the viscosity of a suspension of spherical particles by thermodynamical methods, in a Paper on the determination of the molecular radius, and found the value

$$\eta_e = \eta_0(1+f),$$

which is identical with the formula given on previous page, except for the numerical constant.

This result had been entirely overlooked by colloidal chemists ; although the viscosity of suspensions is discussed both in Freundlich's "Kapillarchemie" and in Ostwald's "Grundriss," no reference is made to Einstein's result in these standard works, both of which appeared in 1909. The formula was, however, noticed in 1910 by Bancelin,[†] who proceeded to test it experimentally on suspensions of gamboge made by Perrin's method, and consisting of particles of uniform size. He found that the linear law held good up to 3 per cent., irrespective of size, but that the proportionality factor was 2·9 instead of 1.

Bancelin drew the attention of Einstein to the divergence in the numerical constants, and Einstein revised his formula and found a new constant, 2·5. The method by which the revised result was obtained has never been published.

A set of determinations of the viscosity of suspensions of starches of different origin (and therefore of different size) was made by Harrison[‡] in 1911. He found that the increase in viscosity was independent of the size of the particles and in linear ratio to the volume as found by centrifuging the suspension and reading the total volume occupied by the granules.

On the other hand, Sven Oden[§] used a sulphur sol and found that the viscosity of more concentrated solutions increases more rapidly than the concentration, and also that the more disperse the sol (the smaller the particles) the greater the viscosity.

It seemed possible that some of these discrepancies were caused by the use of the capillary viscosimeter, and the present investigation was undertaken with Hatschek's modification of Couette's apparatus, which allows of a variation of the rate of shear. This apparatus (Fig. 2) consists of a hollow cylinder A, which is supported by a wire, B, from a heavy bracket, C. The cylinder A is open and bevelled at the end, and is coaxial with an outer cylinder, D. Two short guard cylinders E and E′ nearly closed at one end are placed opposite the open ends of cylinder A, leaving a clearance of about 2 mm. between the bevelled surfaces. The outer cylinder D rests on a table, F, which can be rotated. When the whole is filled with liquid and the outer cylinder is set in motion, a layer 0·5 cm. wide is sheared between the moving and the suspended cylinders. The consequent twist of the suspended cylinder is read by means of a mirror, G, attached rigidly to it above the level of the outer cylinder.

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[*] A. Einstein, "Ann. d. Physik," XIX., 289 (1906).

[†] M. Bancelin, "Koll.-Zeitschr.," IX., 154 (1911).

[‡] Wm. Harrison, "Journ." Soc. Dyers and Colourists, XXVII. (April, 1911).

[§] Sven Oden, "Zeitschr. Phys. Chemie," LXXX., 709 (1912).

With the apparatus, as described so far, the viscosity of water, which from previous experiments is known to be constant within the limits of shear employed, showed a marked increase with rising rates of shear. It appeared that the effect of the revolving bottom of the outer cylinder was not entirely eliminated by the guard "E," but this was finally accomplished by fixing to the latter a thin plate, H, coming to within 1 mm. of the wall of the revolving cylinder. This reduced the increase in viscosity coefficient to 1 per cent. in the case of water and to 2 per cent. in the case of glycerine and water, when the angular velocity, and consequently the rate of shear, was increased between five and six times. Since the inside diameter of the outer cylinder is 11 cm. and the outside diameter of the suspended cylinder 10 cm., each degree of arc in the revolving cylinder is equivalent to 0·0959 cm., and its linear velocity is obviously half the actual rate of shear of the liquid layer per centimetre of depth.

As regards the choice of a suitable suspension, the field is not as large as would appear at first sight. The number of solids obtainable in microscopic particles of even roughly spherical shape is slight, and their specific gravities are mostly well over two.

The suspension finally chosen for experiment was that of rice starch in a mixture of carbon tetrachloride and toluene. Both liquids were bought as pure, and were only prepared by being dried over calcium chloride. The amounts of the two liquids were so adjusted that the starch granules remained suspended for several hours. The specific gravity in the

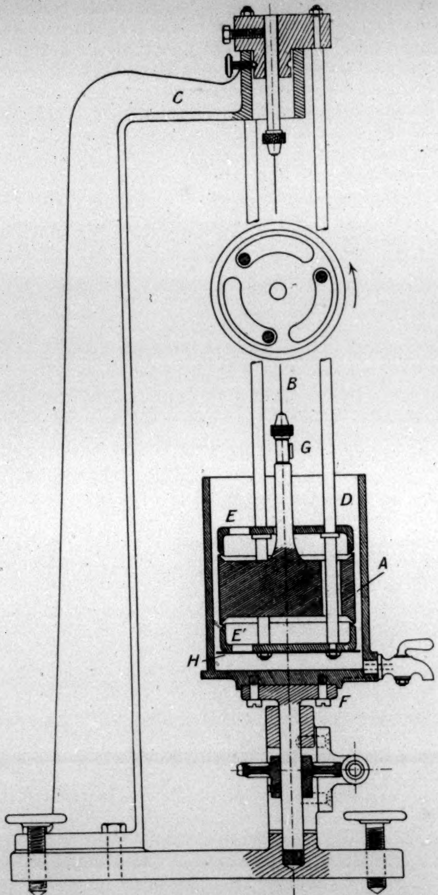

FIG. 2.

final set of determinations was 1·505 at 13°C. The starch used was pure rice starch, the granules of which are not spherical, but polyhedral, often hexagonal in section. By

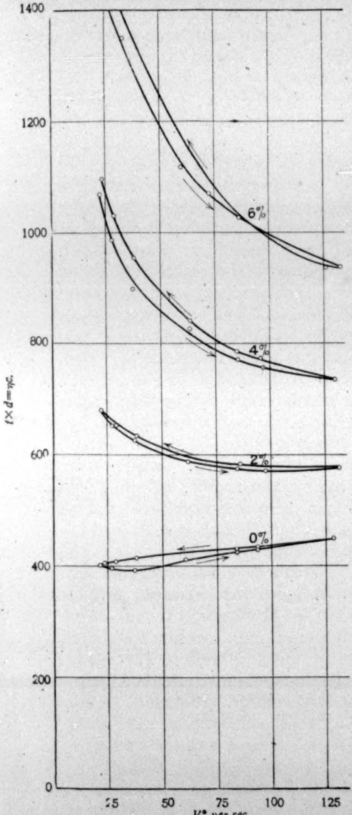

FIG. 3.

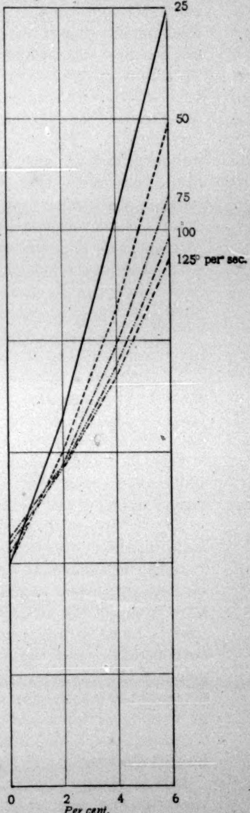

FIG. 4.

constant drying and sieving the larger granules were eliminated and those used finally were about 0·003 mm. in diameter. This starch was prepared by drying it at 100°C.; finally it was sifted and preserved in stoppered bottles, but it evidently took up a certain amount of moisture from the air. Preliminary experiments having shown no difference between old and new suspensions, the ordinary procedure was to make up a litre of the mixture some six to eight hours before the time of the determinations. The mixture was brought if necessary to the required temperature, and put into the viscosimeter. The zero was read and the cylinder rotated at its lowest speed; after a short run to obtain equilibrium, the time of a convenient number of revolutions was taken, and the position of the inner cylinder was read by means of the mirror. After a couple of concordant readings had been obtained the rotation was stopped until the cylinder had come to rest, when these operations were repeated at the next highest speed. After seven speeds had been used the process was reversed until the lowest speed was reached. The whole experiment occupied some two hours. At higher concentrations it was found better to tap the apparatus gently to get the true zero.

The systems treated were the 0, 2, 4 and 6 per cent. suspensions by volume, and the angular velocities varied roughly from 20 deg. to 180 deg. per second, corresponding to linear velocities of the revolving cylinder or 1·9 to 17·2 cm. per second.

Figs. 3, 4 and 5 show the results obtained. In Fig. 3 the products $d \times t$ are plotted against the angular velocities, the curves showing the behaviour for each concentration, while in Fig. 4 these same products are plotted against the concentrations, the curves in this case showing the behaviour of the various suspensions at the same speed. The model combines both of these, and completely defines the viscosity; all possible values of the viscosity (within the limits of the investigation) lie on its surface, the viscosity being a function both of the concentration and the rate of shear. The most noticeable result of the whole set of determinations is the marked dependence of the viscosity on the rate of shear. It is much greater at lower rates, but tends to approach constancy at rates above a certain limit, which limit itself increases with the concentration of the suspension.

This is clearly shown in Fig. 5, which gives the relative viscosities, *i.e.*, the ratio

$$\eta_c/\eta_0 \text{ at same rate of shear}$$

for a number of different velocities. If we use this curve to test the formula

$$\eta_c/\eta_0 = 1 + a \times \frac{\text{volume of disperse phase}}{\text{total volume}},$$

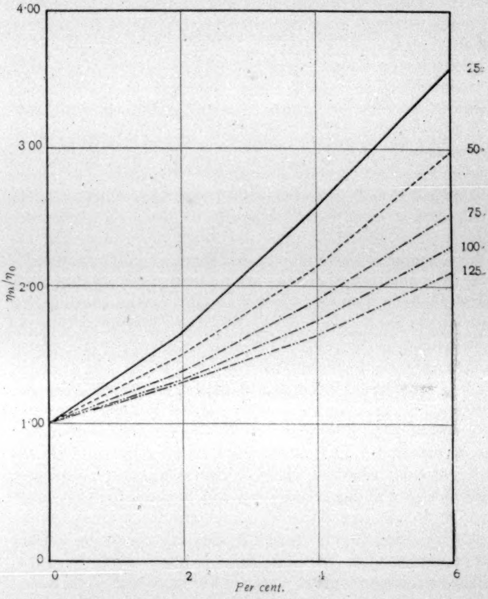

Fig. 5.

we obtain the following values :—

Concentration.	η_c/η_0	a
2 per cent.	1·3	15
4 per cent.	1·6	15
6 per cent.	2·1	18

Which show that at 6 per cent. the increase is more than linear at 125 deg. per second. Moreover, we see by the curves that the 2 per cent. suspension becomes irregular below 75 deg. (7·18 cm.) per second.

The deviations from the formula are, therefore, of two kinds, the increase in relative viscosity is more than linear, especially at low rates of shear, and the proportionality factor is much greater than the figure found theoretically. As regards the latter, the difference between spherical and irregular polyhedral particles may be sufficient to account for the discrepancy.

The more than linear increase probably points to this that the assumption on which both Einstein's and Hatschek's deductions are based—viz., that the particles do not influence one another—is untenable. In a 2 per cent. suspension of such particles as we have considered, the distance between adjoining particles, assuming them to be placed at the corners of cubes, would be less than four diameters from centre to centre or less than three diameters from surface to surface. With smaller particles, which would be correspondingly more numerous for the same aggregate volume, the distances would be considerably smaller still. It, therefore, seems quite possible that each particle will be impeded by the surrounding ones, a condition of things which hardly lends itself to mathematical treatment. If such interference between adjoining particles does take place, it is, however, obvious that both their absolute size and distance—in other words, the degree of dispersity and the concentration—must affect the viscosity of the system.

A possible source of error in the experiments described deserves mention. The starch used still contained imbibed water, and it is, therefore, possible that it was not completely wetted by the medium, a condition which would perhaps cause further and unknown complications. One experiment made with highly dried starch showed a viscosity much lower than could be explained by the decrease in volume due to the withdrawal of a few per cent. of water. We have settled on a suspension free from this defect, and hope to investigate it fully when conditions are more favourable.

We gladly take this opportunity for expressing our thanks to Dr. R. S. Willows for much valuable advice and assistance.

Physical Laboratory of the Sir John Cass Technical Institute.

ABSTRACT.

This investigation was undertaken with a view to testing the Einstein-Hatschek formula at variable rates of shear. According to this formula the viscosity of a suspension of rigid spherical particles grows in linear ratio with the aggregate volume of suspended particles,

and is independent of their size, as long as the latter conforms to Stokes's formula.

The suspension chosen was one of rice starch of 0·003 mm., and less, diameter, in a mixture of carbon tetrachloride and toluene having the same specific gravity. The measurements were carried out in a modification of Couette's apparatus, in which the deflection of a cylinder, suspended coaxially in another cylinder filled with the liquid and rotated at different speeds, is measured. All measurements were carried out at speeds below that at which turbulence sets in, so that the deflection was proportional to the product of viscosity × angular velocity.

The results of the investigation are: (1) The viscosity of a suspension is a function of the rate of shear, and increases as the latter decreases, the difference being more marked at higher concentrations; (2) for all rates of shear the viscosity of the suspension increases more rapidly than the aggregate volume of suspended matter; (3) for any one rate of shear the relative viscosity of a suspension, *i.e.*, its absolute viscosity divided by the absolute viscosity of the medium at the same rate of shear, also increases more rapidly than the percentage of suspended matter, the divergence from the linear increase demanded by the formula becoming less as the rate of shear becomes greater, so that a linear law may possibly hold good at rates of shear higher than those attainable in the present apparatus without turbulence.

The general conclusion is that the assumption on which the Einstein-Hatschek formula is based, viz., non-interference between adjoining particles, is not tenable in the case of suspensions containing between 2 and 6 per cent. of suspended matter.

XXVIII.—*Experiments with Mercury Jet Interrupters.* By Capt. C. E. S. Phillips, *F.R.S.E.*

Received June 28, 1916.

The following experiments have been undertaken with a view to ascertaining what is the form of the mercury column issuing from a hole in the side of a rotating drum that is continuously supplied with mercury by centrifugal action.

Incidentally, some improvements in the general design of interrupters have suggested themselves.

The wide use now made of this method of regularly "making" and "breaking" the current in the primary circuit of induction coils points to the need for some such investigation as I have attempted, in order to increase, if possible, the efficiency of this important part of an X-ray equipment.

It was necessary, of course, that observations should be made within the interrupter itself while in action, and the following apparatus was therefore constructed. (Fig. 1.)

The working parts of the arrangement are contained in a cast-iron vessel, V, which stands firmly upon the wooden frame F, and measures 6 in. high and 7 in. in diameter.

It is closed at the top with an easily removable lid, which is fastened down upon a rubber washer by means of thumb screws.

The glass window G enables the drum D and the segments S S′ to be seen while the interrupter is at work.

The revolving drum is attached to a spindle which passes down through the steel bush B and makes mechanical connection with the motor M, as shown in the figure.

The lower part of the drum dips into mercury held in the well W, and a small hole drilled in its base close to the spindle allows the liquid to enter.

The drum itself is made of vulcanite, for reasons to be given later, and so requires, on account of its buoyancy, to be held down under the mercury by the spring connection to the motor shaft. No foot bearing is therefore necessary, nor can gas escape through the sleeve, on account of the mercury seal.

The walls of the drum are parallel on the outside, but thicker at the base than at the top, and two holes, H H′, 1·5 mm. in diameter, are drilled opposite to each other in the vulcanite to allow the mercury to escape when driven upwards by centrifugal force.

A rim at the top serves to prevent loss of mercury by spilling at excessive speeds, and assists in maintaining a good supply of mercury at the orifices H H′.

The metal segments S S′ are arranged symmetrically, as shown. They are capable of adjustment as to width, and are connected in series with the circuit which it is required to interrupt.

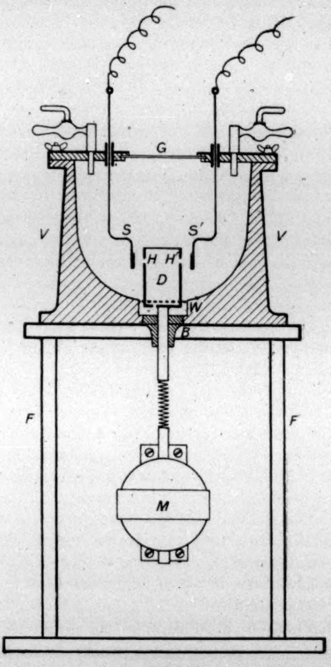

FIG. 1.

Taps are provided for the introduction of gas, and a small disc shutter is arranged to close the window in the lid when necessary. This apparatus is convenient for comparing the effect of varying the size and form of the orifice through which the mercury issues, for observing the advantage, or otherwise, of changing the distance of the segments from the drum, or altering their shape, angle, or the material of which they are made. It is also useful for testing the efficiency of various volatile liquids introduced for the purpose of cutting down the flare due to the self-induction of the circuits usually dealt with.

The Form of the Mercury Column.

When the interrupter is in action it is seen that two bright arcs occur at each segment, one at the point where the mercury first impinges, and the other where the mercury column leaves the sharp edge. When a current exceeding 2 amperes is passed by the apparatus while connected to an induction coil, the second arc is markedly greater than the first, owing to the self-induction of the circuit, and if the current is still further increased a flare begins to develop where the mercury leaves the segment.

The arcs at "make" always occur with great regularity, but the current passed by the apparatus often becomes fluctuating as soon as flaring takes place at the moment of "break."

The two mercury columns are illuminated by both the arcs at "make" and the flares at "break," and since, for small currents, these always occur when the orifices are exactly in the same position relatively to the segments, the mercury columns may be easily observed, and appear to be stationary no matter how rapidly the drum is revolving.

In this way it is noticed that the mercury seems to pour out of the side of the drum in a continuous stream, and that its path is bent backwards.

A little consideration, however, will show that this is not a correct interpretation of the phenomenon.

For if the direction of rotation of the drum is clockwise, as shown in Fig. 2, we may imagine, for the sake of simplicity, that the mercury escapes from the hole H at regular intervals; that is to say, when the orifice has moved into the positions marked A, B, C, D, E, F respectively. At the moment when the mercury escapes from the orifice at A it is moving in a circular path with the velocity of the drum itself, so that if at the instant the mercury is free the radial component is nil (and in the case considered it is very small), the mercury, on appearing through the orifice, will move off along a line, AO, which is a tangent to its original path. By the time that the orifice has reached the position F the mercury, if we disregard air resistance, will have reached the point 5 along AO, the length of A5 being equal to the circular arc AF.

Similarly, the mercury emitted when the orifice is at B will at the same instant have reached the point 4 along the line BO′, and the portion coming from the orifice when it is at C will reach the point 3 along the line AO″, and so on.

If, now, these points are joined together, a curve is obtained which is seen to resemble closely that observed through the window of the interrupter when the mercury column is rendered visible by the intermittent illumination occurring at the segments. But in actual practice the mercury flows out constantly through the orifices in the drum, with the result that continuous columns are produced which sweep round and serve the purpose of " making " and " breaking " the circuit. It must be borne in mind, however, that these columns are to be regarded as consisting of an infinite number of elements of mercury moving out from the drum tangentially, and therefore in directions normal to the concave aspect of the resulting curves. Under ideal conditions the columns would take the form of an involute of the circle represented by the drum's circumference.

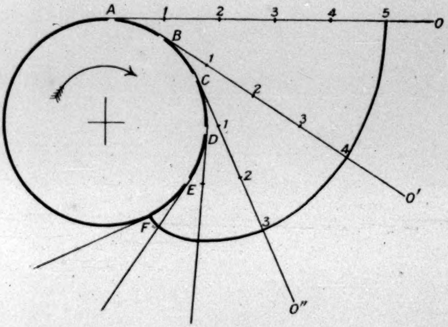

FIG. 2.

Fig. 3 is a photograph of one of the columns taken by the light of the small arc that occurs at "make."

In cases where the drum is provided with radial jets the form of the curve becomes slightly modified.

Fig. 4 represents the breaking up of the column into globules which, in separating from one another, interrupt the current with great suddenness at the point where the mercury leaves the segment. High surface tension is of importance here, and it is, therefore, essential to keep the mercury not only apparently clean, but actually as pure as possible.

This is also advisable on account of the fact that a very small amount of contamination due, for instance, to the presence of a trace of soluble metal, strongly increases the tendency of the mercury to oxidise.

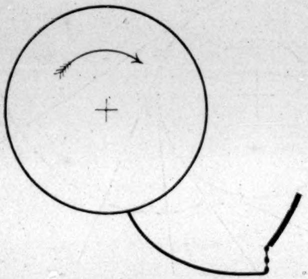

FIG. 4.

I have, therefore, tried to find a metal which would be more suitable for the segments than the copper in common use, and, so far, the most successful results have been obtained with tantalum.

This substance is not "wetted" by the mercury, it remains bright and clean indefinitely; it is easily worked and its high melting point renders it very durable.

Its one objection at the present time is comparative rarity and high cost.

The interrupter which is shown at work to the Society is fitted with tantalum segments, and it will be seen that the last 3 mm. at the edge where the mercury leaves are turned abruptly towards the drum to ensure greater regularity of action.

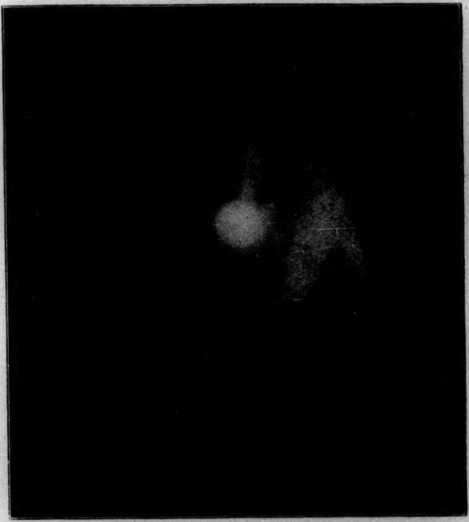

FIG. 3.

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Experiments upon the best distance at which the segments should be placed show that the resistance of the mercury column is very appreciable, and that the interval between that portion of the segment where the break occurs should not be more than $\frac{3}{16}$ in. from the drum.

By placing the segments so that their curvature conforms to that of the mercury column itself the "make" current would be diminished somewhat owing to the greater length of the mercury initially intercepted by the segment. In X-ray work it seems desirable to check the rate of growth of the current in the circuit and this point may, therefore, be of some practical use.

Experiments with differently shaped orifices in the drum vertical slits, horizontal slits, &c., of various sizes have given no better results than can be obtained with the usual hole of about 2 mm. in diameter. It does not seem to matter, in fact, how much larger the hole is than this, for the mercury column appears to be approximately of the same thickness in spite of increased diameter of the orifice; nor with a long vertical and narrow slit can a ribbon of mercury be obtained. In extreme cases several small columns may appear, but never a ribbon. Consideration of Fig. 2 and the explanation given of it will show that this result is to be expected. Thicker columns can, however, be obtained by enlarging the holes in the drum, and covering them with short tangential tubes closed at one end and drawn down somewhat at the other, but with a large opening in their sides in register with those in the drum. If a good supply of mercury can be delivered to such tubes they can be arranged to emit a stream of any required diameter.

One common fault of modern mercury interrupters is the poor insulation of the jets in the region of the orifice. It is customary to use radial arms of metal connecting with the mercury in the well, and requiring insulating shields round the orifices to prevent irregular contacts due to back-splash. In the interrupter which I have described this is avoided by employing as rotating drum a vulcanite cylinder so that the back-splash from the segments, provided it is not allowed to interfere with the continuity of the column itself, a simple matter, is entirely prevented from producing irregularities.

Finally, some experiments have been carried out with a view to finding a substitute for coal gas (which is not always available) in reducing the flare that occurs at the moment of "break."

Of all the volatile liquids tried, ether was found to be by far the most effective.

The exceptional behaviour of coal gas, hydrogen or ether is a matter of interest, and the usual explanation depending upon the high specific heat of hydrogen certainly cannot apply in the case of ether. It may be that the action has to do with changes of a totally different nature occurring in either substance, or that their effectiveness depends upon a possibly increased surface tension of the mercury in their presence.

An attempt to work the interrupters under compressed air has not proved a success up to a pressure of five atmospheres.

If it is desired to employ a very heavy current, recourse must be had to multiple jets, and by that means as much as 40 amperes at 200 volts can be safely passed by interrupters suitably designed for the purpose.

In conclusion, I wish to express my thanks to Mr. F. Rowe, who has kindly assisted at these experiments, and who has himself made most of the necessary apparatus.

ABSTRACT.

The Paper describes an experimental attempt to ascertain the form of the mercury column issuing from a hole in the side of a rotating drum, that is continuously supplied with mercury by centrifugal action.

Incidentally a new form of interrupter is introduced, in which the interior is visible through a window in the lid. The arrangement forms a suitable apparatus for experiments with various forms of orifices and metallic contact segments, and the Paper gives an account of work in that direction. As it is important to ensure the cleanliness of the mercury in interrupters of this type, the usual copper segments are replaced by ones made of tantalum, which, for many reasons is preferable. It is not " wetted " by mercury, it remains clean and bright indefinitely, and its high melting point renders it lasting.

Experiments with various forms of orifice are described, and it is pointed out that the issuing stream is only slightly affected by this means. An explanation is given of the fact that a vertical slit orifice will not produce a ribbon of mercury, and that no matter how much the diameter of the orifice is increased beyond about 2 mm., the cross section of the mercury column remains unaltered. A method is described, however, by which a much larger stream of mercury can be obtained from the rotating drum, if necessary.

Brief reference is made to experiments with various volatile liquids in suppressing the flare which occurs when the mercury columns leave the contact segments. The three well-known substances which are most effective in this respect are coal gas, hydrogen and ether.

It is pointed out that experiments of this nature are necessary, in view of the wide use now made of mercury interrupters in X-ray work.

DISCUSSION.

Capt. **Reid** thought the instrument described by the author was of considerable importance. In practice it would be a great advantage to see the interior of the instrument when anything went wrong.

Dr. R. S. **Willows** congratulated Capt. Phillips on having broken new ground in his experiments. Mercury interrupters had not been very scientifically investigated so far. He thought experiments on the thickness and resistance of the jet, on the resistance at the contact with the tantalum vane, and on the effect of varying the inductance of the primary circuit on the performance of the interrupter, would yield results of importance. Had the best shape and inclination of the plate on which the jet impinged been worked out ? With regard to the effect of different gases in quenching the flare, he thought the specific inductive capacities were the determining factor rather than the specific heats. The same problem was met with in running a singing arc.

Mr. G. L. **Addenbrooke** mentioned that one firm he knew of made interrupters with an electrode of variable inclination.

Mr. P. R. **Coursey** (communicated remarks): The author has touched upon one of the main difficulties encountered in practical work with the modern forms of mercury break, viz., that it is usually quite impossible to inspect the operation of the break while it is in use, or to see at once what is wrong if it does not work satisfactorily, without in many cases completely dismantling the apparatus. In some experiments which I carried out some time ago upon the subject, a special form of break* was constructed both with this object in view and for the purpose of handling fairly heavy currents. The whole of the working parts are carried by an insulating top supported on a stout glass jar, and may therefore be easily lifted out bodily when required by releasing the clamping screws, while at the same time the operation of the break is always open to view. Various sized jets up to about 4 mm. diameter (the full bore of the pump holes) were employed in different experiments, but as is pointed out in the Paper, little advantage is shown by the large jets, as compared with the small ones, owing to the tendency of the jet to break up from a solid stream into separate globules, unless the gap between the jet hole and the fixed electrode is kept very small. When this is the case it becomes almost essential to keep the electrode surface concentric with the exterior of the pump, as otherwise small clearances cannot be maintained. The author's method of securing a solid jet is particularly interesting in this connection. Considerable improvement in the operation of mercury interrupters, and elimination of the sparking at the contacts, may usually be secured by electrically tuning the discharge circuit to approximately the same frequency as that of the interruptions by means of a condenser connected either directly across the interrupter terminals, or, preferably (especially with a supply of 100 volts or more) across both the interrupter and induction coil primary in series. A suitable choking inductance and resistance must be inserted in the supply leads with this arrangement. The value of the inductance in series with the interrupter is usually of considerable importance in securing maximum output, and most satisfactory and steady operation of the break with the minimum of internal sparking, and the value that is most suitable is best found by trial in each case, its action in conjunction with the condenser being to control the rate of rise and fall of the current, so that the circuit is broken in each case at the most favourable point on the current wave. These arrangements, by reducing the sparking, lengthen the time during which the interrupter can be used before cleaning of the mercury becomes necessary.

Capt. **Phillips**, in reply, said that some of the points raised by Dr. Willows were dealt with more fully in the Paper than in his description.

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* "Electrician," Vol. LXIX., p. 899, 1912.

The resistance of the jet was a very interesting point, and he had some experiments in progress on the matter. He was not quite clear whether he seat of the resistance was the mercury column or the junction of the column with the electrode. The position of the electrodes was also dealt with in the Paper.

In reply to Mr. Coursey: The interrupter devised by Mr. Coursey recalls that introduced some 20 years ago by Dr. Max Levy, which was also enclosed in a glass cylinder. Mr. Coursey does not say if his interrupter is required to work in an atmosphere of coal gas, but I presume that to be the case, and it is therefore open to the objection that if by accident an explosion occurs within, the whole apparatus is shattered. The window in the instrument exhibited may be made of non-flam celluloid, and is replaced in a few minutes if necessary. It is also desirable to be able to look down on the stream rather than to view it from the side. I am very interested in Mr. Coursey's references to the use of capacity and inductance in the interrupter circuit, and think that further experiments in this direction would be worth while.

XXIX. *A Sensitive Magnetometer.* *By* P. E. SHAW, *B.A.*, *D.Sc.*, *and* C. HAYES, *B.Sc.*

RECEIVED MAY 22, 1916.

IN a research recently published by one of us* there is a description of a torsion balance of special delicacy for gravitation research. A diagrammatic representation of this apparatus is shown in Fig. 1. A fibre, *FF*, 600 mm. long, 15μ diameter, carries a beam, *B*, 35 mm. long, from the ends of which are

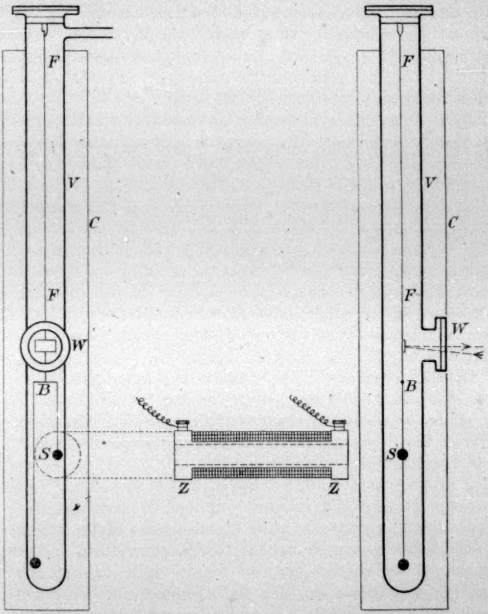

FIG. 1.—FRONT AND SIDE VIEWS OF THE MAGNETOMETER.

The axis of the solenoid is, as shown, in the first case perpendicular to the plane of the paper and in the second case in the plane of the paper.

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* "The Newtonian Constant of Gravitation as Affected by Heat," Shaw, "Phil. Trans.," 1916, A. Vol. CCXVI., p. 349.

hung, by fine wires of length 150 mm. and 350 mm. respectively, two small spheres of silver, each weighing about 3 gm. This torsion system is hung in a low vacuum of about 15 mm. pressure. The movements of the torsion beam, carrying a mirror which reflects a distant scale, are observed through the window *W* by a powerful telescope distant about 4½ metres. The vacuum tube *V* is wrapped by several layers of cotton-wool, and this latter is surrounded by a helix of lead "compo" tubing. The cylindrical envelope *C* encloses the cotton-wool and tubing, and all the vacuum tube except the extreme upper portion. The lead helix contains cold water. Further details of this apparatus are given in the Paper quoted.

In the course of the research mentioned it was necessary to heat the vacuum tube. This was attained by the passage of a current through a coil of wire wrapped on the outside of the vacuum tube. It was found later that on account of the field thus produced the silver spheres had become permanently but weakly magnetised with vertical axes. This permanent magnetisation was observed as follows: When the *N*. pole of a bar magnet, 20 cm. long, was brought to about 6 cm. from one sphere, the latter moved, and a scale deflection of several centimetres (right or left, according as the pole was above or below the sphere) was observed. The coercivity was considerable; the field required to remove the permanent magnetism from the spheres being of the same order as that used in its production. After much trial the required field was obtained, and the vertical permanent magnetism was so far removed that the scale deflection due to the presence of the *N*. pole, was reduced to less than 0·5 mm.

The spheres were of silver of the highest purity from Messrs. Johnson, Matthey & Co., who described it as "absolutely pure." Care was taken, during the mounting of the spheres on the torsion system, to avoid any contamination of their surfaces. Clean hands were used by the operator, and after mounting and before entering the vacuum tube, they were washed in nitric acid, followed by distilled water.

This behaviour of such pure silver came as a surprise. One did not expect either silver or the small amount of residual iron to display permanent magnetism and great retentivity. So an investigation was commenced to ascertain the nature of these effects.

Some scraps of the same silver as used for making the spheres were analysed. Specially pure nitric acid was tested, and found by the ferrocyanide test to be free of iron. The silver scraps were then dissolved in this nitric acid. After boiling off any excess of acid, iron-free hydrochloric acid was added, and the silver chloride precipitated. The iron was left in the solution, which was now tested by the colorimetric ferrocyanide test. The result of the analysis was that the proportion of iron to silver was found to be 30/1,000,000. The silver spheres were probably much purer than the scraps used in the analysis, as the latter were the turnings from the spheres.

After searching for authorities on the subject of the susceptibility of the less magnetisable elements, the work of Honda* was taken to be the best on silver up to date. The method employed by Honda was to place a small quantity of the silver in a capsule carried by a torsion beam and to observe the couple produced on the beam when a very powerful field was applied by an electro-magnet near the capsule. He then deduced that the susceptibility of silver is $K = -2 \times 10^{-6}$ c.g.s.

In order to observe the effects of a field on our suspended silver spheres, we brought up a solenoid, **ZZ**, of length 38·5 cm., outside diameter 10·8 cm. and having 528 turns of about 16 S.W.G. copper wire, close to the vacuum tube, opposite to the upper sphere *S*, so that the axis of the solenoid was horizontal, and passed through the centre of the sphere. On passing currents through the solenoid and an ammeter, the field developed at the sphere was varied from 1·3 gauss to 12·0 gauss. The silver sphere being in a divergent field, was urged along the axis of the solenoid and a scale deflection was read by the telescope. As silver is diamagnetic we expected that the sphere would be repelled. But, on the contrary, there was an attraction to the solenoid. Thus, there must be, apparently, sufficient iron impurity present to give it a preponderating effect over the diamagnetic silver. For fields of about 5 gauss, iron has a susceptibility of about 170 c.g.s. Then, supposing silver and iron act independently in a magnetic field in the presence of one another, the proportion of iron to silver in our sphere must considerably exceed 1 to 80,000,000. But we have no authority for supposing that this principle of proportionality holds good. The experimental evidence is, in fact, that the iron loses some or all of its magnetic power when melted into other metals. To quote two examples of this principle :—

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* "Ann. der Physik.," XXXII., pp. 1027-1063.

1. A certain alloy of iron and nickel can be made, which has practically no ferromagnetic qualities. Thus each of these strongly magnetic metals loses magnetism through the presence of the other.

2. Honda* found that for *very large fields* the magnetic influence of the iron impurity is never more than 50 per cent., and sometimes as little as 5 per cent. of that which it would be on the basis of proportionality.

After obtaining the above preliminary result, the current in the solenoid was varied from 2 to 9 amperes (Table I.) and the scale deflections noted. Next, the solenoid was moved along its axis nearer to the silver sphere, and the experiment repeated with the currents 1 to 9 amperes (Table II.). Details as to the form and use of the torsion balance will be found in the gravitation research, as quoted.

TABLE I.

Current. Amps.	Field H.	$\frac{\partial H}{\partial x}$	d_1. mm.	d_2. mm.	$K_a \times 10^6$.
2	1·81	0·40	2·24	0·49	0·176
3	2·72	0·46	4·83	2·45	0·272
4	3·63	0·60	8·43	4·53	0·277
5	4·53	0·80	12·33	8·20	0·264
6	5·44	0·98	17·37	12·00	0·258
7	6·35	1·14	23·35	17·17	0·262
8	7·25	1·30	28·50	21·45	0·248
9	8·16	1·42	35·23	28·78	0·258

TABLE II.

Current. Amps.	Field H.	$\frac{\partial H}{\partial x}$	d_1. mm.	d_2. mm.	$K_a \times 10^6$.
1	1·34	0·29	1·17	0·17	0·159
2	2·67	0·57	4·98	2·03	0·214
3	4·01	0·72	10·65	6·30	0·274
4	5·34	1·14	21·13	12·28	0·256
5	6·68	1·45	28·15	20·93	0·236
6	8·02	1·76	39·95	31·25	0·235
7	9·35	2·02	53·93	42·10	0·237
8	10·69	2·29	71·91	59·39	0·250
9	12·02	2·59	88·19	75·31	0·245

It should be observed that care was taken throughout to have the silver sphere in a cyclic state. Before commencing the readings in Table I. the largest field about to be used was developed in the solenoid, and this field was slowly reduced with alternations until it became zero. Again, before every reading, direct or reverse, the current in the solenoid was reversed, say, 10 times.

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* *Loc. cit.*

To Find a Value for the Susceptibility of the Silver Used,

Let

K=Susceptibility of absolutely pure silver.
K_a=Susceptibility of the (impure) silver used.
V=Volume of the sphere.
a=Arm of the torsion balance.
G=Couple required to produce a deflection of 1 mm. on the scale. (In this apparatus G has the small value $4{\cdot}5\times 10^{-7}$ dyne cm.)
P=Permanent magnetism (this is a magnetic moment).

Then the sphere is in a divergent field whose gradient along the axis of the solenoid is $\partial H/\partial x$; and we have then—

For a Direct Current—

Couple acting on torsion balance

$$=(VK_aH+P)\,H/\partial x\,.\,a=G\,.\,d_1, \quad . \quad . \quad . \qquad (1)$$

where d_1=scale deflection.

For a Reverse Current—

$$\text{Couple}=(VK_aH-P)\partial H/\partial x\,.\,a=G\,.\,d_2, \quad . \quad . \quad . \qquad (2)$$

where d_2=scale deflection.

Whence—

$$K_a=\frac{G(d_1+d_2)}{2VH\partial H/\partial x\,.\,a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

The value of H is calculated from the usual expression—

$$H=2\pi ni(\cos\beta-\cos\alpha),$$

and $\partial H/\partial x$ is calculated from a graph for H/x, specially drawn for the purpose.

The last column in Tables I. and II. show the values of K_a, ascertained from equation (3). Notice that the values of d_1 and d_2 differ considerably, showing that the permanent magnetism is an important factor.

The results for $H-K_a$ are shown in Fig. 2. It will be seen that the value of K_a rises with an increasing field, and attains a maximum for a field $H=3{\cdot}0$ gauss. This is the field which gives the maximum susceptibility for pure soft iron, and we might expect that, since the value of K for iron drops rapidly as the field increases thereafter, the curves in Fig. 2 would also drop rapidly. But, in fact, the value of K_a is practically constant with increasing field. This means that, at least for fields of 3·0 to 9·0 gauss, either the values of K for iron and for silver vary together, or neither of them changes. Supposing (as is generally done) that the susceptibility of *pure* silver is constant, then that for the iron impurity is also constant over this range.

Honda worked with the range of field 5 to 23 kilo-gauss, and in the case of the slightly impure silver used, he found only a small change in the susceptibility (at most about 30 per cent. of the whole) for this range. The proportion of iron to silver in his specimens was about 6/1,000,000 (as shown by chemical analysis). For these fields the effect was diamagnetic—*i.e.*, the silver effect preponderates over that of the iron. This again is another disproof of any simple superposition theory, as the figures for purity and susceptibility show.

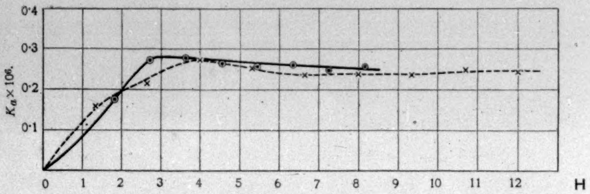

FIG. 2.—CURVE SHOWING THE RELATION OF FIELD IN GAUSSES TO APPARENT SUSCEPTIBILITY $\times 10^6$.

For the very large fields used, Honda found a hyperbolic relation—

$$\chi=\chi_\infty+\sigma/H,$$

where

χ=Specific susceptibility for the silver specimen in a field H.

χ_∞=Specific susceptibility for an infinite field.

σ=A constant, the specific intensity of magnetisation for the iron impurity.

In our experiments there is no trace of a hyperbolic relation; in which case σ, in the above expression, is not constant, but variable.

Two researches other than that of Honda should be noticed:—

(1) A. P. Wills* worked on weakly magnetic bodies with fields of 1 kilo-gauss and upwards. He failed to establish any permanent magnetic state in the substances used. For these high fields the permanent magnetism would have been very small in proportion to the temporary magnetism, and in any case would be imperceptible, except with such a delicate instrument as was used by us.

(2) Fleming and Dewar† worked on silver at low temperatures for high fields only (2 to 3 kilo-gauss).

The above are the only recent researches at all kindred to ours which we have discovered.

It would have been interesting to extend the investigation by increasing the field and by varying the purity of the silver sphere, but as the torsion system was required for further research on gravitation (*see* introductory remarks), the vacuum could not be opened, and the investigation extended. We are thus forced to leave the problem at this stage, having satisfactorily tested the magnetic qualities of the spheres for low fields, which alone are important as regards the gravitation research.

We suggest that on a torsion balance of extreme delicacy such as that used by us (which is about 10^6 times as sensitive as that used by Honda), it would be possible to carry out a systematic investigation of the magnetism of feebly magnetic materials even for weak fields. This would be untrodden ground.

ABSTRACT.

A torsion balance of extreme delicacy carries a pair of purest silver balls, each 3 gm. weight. A solenoid with horizontal axis passing through one of the silver balls, is brought close to the balance. On exciting the solenoid, divergent fields of known strength are obtained in the region of the ball. The resulting attraction of the ball to the solenoid is shown by a mirror reflecting a distant scale to a telescope. The couple on the torsion beam required to produce 1 mm. scale deflection is 4.5×10^{-7} dyne cm., and this torsion balance is 10^6 times as sensitive as any known to have been used previously in this kind of work.

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* "Phil. Mag.," May, 1898.

† "Proc." Roy. Soc., p. 311, 1898.

The results of these experiments are :—

1. The magnetic properties of the silver are ascertained even for weak fields of 1 – 10 gauss.

2. The silver has a pronounced retentivity ; this effect being presumably due to the small trace of iron impurity.

3. The relation of susceptibility of the silver to the field used is found. The susceptibility of each of the constituent materials (*a*) pure silver, (*b*) residual pure iron, appears to be greatly modified by the presence of the other material.

DISCUSSION.

Dr. S. W. J. Smith thought that the results obtained by the authors, showing the susceptibility of nearly pure silver in weak fields, were both interesting and instructive. He thought the authors, in discussing their significance, had overlooked the fact that the minute amount of iron (not exceeding 30 parts per million) shown to be present by chemical analysis, would not have the same effective susceptibility as iron in the form, for example, of long rods magnetised in the direction of their length. It was true that iron, when alloyed with other substances, could lose its characteristic ferromagnetic properties ; but there was no reason to suppose that it would do so when present in silver, except in so far as the properties of a very minutely divided substance might differ from those of the same substance in bulk. So far as he knew, iron and silver were mutually insoluble. In that event the impurity found to be present should be regarded as minute particles of iron scattered about in a matrix of silver. To obtain an approximate idea of the effect of these particles upon the susceptibility of the material as a whole, it would be sufficient to regard them as spheres. Since the apparent susceptibility of a sphere is equal to $K/(1+\frac{4}{3}\pi K)$, where K is the true susceptibility, and since the true susceptibility of iron in weak fields is considerable, the apparent susceptibility of such spheres would be practically constant in weak fields and equal to $3/4\pi \doteqdot 0{\cdot}24$. Hence, if the fraction of the total volume occupied by the iron were $n \times 10^{-6}$, the observed susceptibility of the material would be of the order $K_a = (0{\cdot}24n - 2)10^{-6}$, where -2×10^{-6} represents the susceptibility of the silver. It was found by the authors that the susceptibility was practically constant over the range $H=4$ to $H=12$ c.g.s., and approximately equal to $0{\cdot}25 \times 10^{-6}$. This would agree with $n \doteqdot 9{\cdot}4$. In other words, the results would indicate that the amount of iron present as impurity was of the order 10 parts per million (by volume). The curves given by the authors seemed to show that the apparent susceptibility varied considerably in fields lower than $H=4$; but part of the appearance of variability was due to the fact that, by inadvertence, the curves had been made to pass through $K_a=0$ at $H=0$. A possible source of uncertainty in the measurements in the weaker fields was the relatively great importance, under these circumstances, of P, the (assumed) permanent magnetism of the sphere. It seemed unlikely that the value of K for the iron in the weaker fields would be such as to make the effective susceptibility much less than $3/4\pi$, although there would be some tendency in this direction. The conclusion which he would draw from the data would be that the magnetic analysis of the material agreed with the chemical analysis and supported the inference, from other experiments, that iron and silver are mutually insoluble. The results obtained in strong fields (by Honda and others) did not, as the authors suggested, conflict with this conclusion, but confirmed it. The diamagnetic susceptibility of silver probably remains constant as the field strength is increased (within experimental limits) ; but, in intense fields, the susceptibility of iron is small compared with $3/4\pi$. For instance, in fields of the order 25,000 c.g.s., the value of K may be of the order 0·1 to 0·05. Taking the latter figure, the effective susceptibility of the iron spheres would be approximately 0·04. The observed susceptibility of the material as a whole would be of the order $K_a=(0{\cdot}04n-2)10^{-6}$. Hence, assuming the value of n already deduced, we should expect K_a to be of the order $-1{\cdot}6\times10^{-6}$. Therefore, we should expect that the material used by the authors would become diamagnetic in strong fields. That it would, in fact, behave in such fields like the silver, of similar purity, examined by Honda.

Dr. CHREE said it was of the utmost importance in working with weak fields to get rid of effects due to electric tram and railway systems. This was not an easy matter nowadays. He had expected to hear some reference to the bearing of these results on Dr. Shaw's gravitational experiments, and would like to know if the magnetic experiments had caused any modification in Dr. Shaw's conclusions on the effect of temperature on gravity.

Prof. BOYS said that in his own experiments on gravitation, and also in the design of the radio-micrometer, the magnetism of impurities had always to be considered. The magnetic forces involved are so minute, that in most instruments—galvanometers, for example—they are ignored. In the radio-micrometer the field that could be employed was limited by the magnetism of the purest copper that could be obtained. He had drawn some copper himself which, after being cleaned with acid and gilt to protect it from air, had worked very satisfactorily. In the case of his gravitation experiments, he had used gold balls of the greatest purity the Mint could supply, cleaned with nitric acid. No consistent magnetic disturbances were detected on moving a permanent magnet about in their neighbourhood.

Dr. SHAW, replying for the authors, was gratified that Dr. Smith's calculations had confirmed their numerical results. His theoretical treatment had been very instructive, and had enlightened them on several important points. He would like to ask Dr. Smith if superposition of magnetic properties would still occur in the case of two mutually soluble metals ?

Dr. SMITH : In general, no.

Dr. SHAW, continuing, said, in reply to Dr. Chree, that in order to test whether the magnetic force between the large lead spheres and the silver spheres would vary appreciably with temperature in the gravitational experiments, he had inserted an iron bar in one of the lead spheres, but even then he had been unable to detect any variation in the force exerted on the silver when the lead and its contained rod were heated to 200°C. Since the magnetic material in the lead was very much less than this in the actual gravitation experiments, it was certain that the results were not affected by thermo-magnetic phenomena.

XXX. *The Latent Heat of Fusion of a Metal and the Quantum-Theory.—II. By* H. STANLEY ALLEN, *M.A., D.Sc., University of London, King's College.*

RECEIVED MAY 19, 1916.

§1. IN the first part of this Paper, read before the Society on May 12, 1916, I discussed the application of the quantum-theory to the calculation of the latent heat of fusion from the point of view of Einstein and also of Debye. The present communication contains a criticism of a theory of the process of fusion recently put forward by Ratnowsky.* Apart from the fact that the theory is based on a number of assumptions, several of which are open to serious objections, it will be shown that some of the results are rendered incorrect by an error in the mathematical analysis.

§2. *The Theory of Ratnowsky.*—The author of the theory considers the entropy of a substance in the solid, and also in the liquid state. He assumes that the whole internal energy, U_N, of the gram atom is made up of two parts, the vibrational energy E_N and the potential (volume) energy $f_N(v)$, so that

$$E_N = U_N - f_N(v).$$

By employing Boltzmann's equation, the entropy is determined by the formula†

$$S_N = \Sigma k\left\{\left(1+\frac{U-f(v)}{h\nu}\right)\log\left(1+\frac{U-f(v)}{h\nu}\right)-\frac{U-f(v)}{h\nu}\log\frac{U-f(v)}{h\nu}\right\}.$$

The temperature T is given by the fundamental relation $\frac{\delta S}{\delta E}=\frac{1}{T}$, from which it follows that

$$U=\frac{h\nu}{e^{h\nu/kT}-1}+f(v).$$

The entropy may then be obtained in the form

$$S_N=\Sigma k\left\{\frac{\xi}{e^{\xi}-1}-\log\left(1-e^{-\xi}\right)\right\},$$

where $\xi = h\nu/kT$.

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* Ratnowsky, "Deutsch. Physikal. Gesell. Verh.," Vol. XVI., p. 1033, 1914.

† In the first part of my Paper Boltzmann's constant, the gas constant for a single molecule, was represented by R. It is preferable to denote it by k, and to reserve R for the gas constant for one gram molecule.

The summation for various frequencies is carried out by assuming with Debye that the number of vibrations within a vibration interval $d\nu$ is equal to $9N\nu^2 d\nu/\nu_m{}^3$, where ν_m is the maximum vibration frequency, and N the number of atoms per gram atom. Then, putting $h\nu_m/kT=x$,

$$S_N=\frac{9Nk}{x^3}\int_0^x\left\{\frac{\xi}{\epsilon^\xi-1}-\log\left(1-e^{-\xi}\right)\right\}\xi^2 d\xi.$$

Integration by parts reduces the expression to the form

$$S_N=\frac{3Nk}{x^3}\left\{4\int_0^x\frac{\xi^3 d\xi}{e^\xi-1}-x^3\log\left(1-e^{-x}\right)\right\}.$$

§3. Ratnowsky then proceeds to deduce an expression for the entropy for small values of x, of the form

$$S_N=3Nk\left(\frac{4}{3}-\frac{1}{2}x-\log x\right).$$

This expression appears to be incorrect, in consequence of the omission of a term in the expansion of $\log(1-e^{-x})$.

It is known that (Bernoulli's series)

$$\frac{1}{\epsilon^\xi-1}=\frac{1}{\xi}-\frac{1}{2}+\frac{B_1}{2\,!}\xi-\frac{B_2}{4\,!}\xi^3+\ldots\quad(-1)^{n-1}\frac{B_n}{(2n)\,!}\xi^{2n-1}\ldots$$

where $B_1=\frac{1}{6}$, $B_2=\frac{1}{30}$, &c.

The series is convergent for values of the variable which are (numerically) less than 2π.

Now $$\frac{d}{d\xi}\log\left(1-e^{-\xi}\right)=\frac{1}{e^\xi-1}.$$

Hence, by integration,

$$\log\left(1-e^{-\xi}\right)=\log\xi-\frac{\xi}{2}+\frac{B_1}{2\,!}\frac{\xi^2}{2}-\frac{B_2}{4\,!}\frac{\xi^4}{4}\ldots(-1)^{n-1}\frac{B_n}{(2n)\,!}\frac{\xi^{2n}}{2n}\ldots$$

Again,

$$\int_0^x\frac{\xi^3 d\xi}{e^\xi-1}=\int_0^x\left(\xi^2-\frac{\xi^3}{2}+\frac{B_1}{2\,!}\xi^4-\frac{B_2}{4\,!}\xi^6\ldots(-1)^{n-1}\frac{B_n}{(2n)\,!}\xi^{2n+2}\ldots\right)d\xi$$

$$=\frac{x^3}{3}-\frac{x^4}{8}+\frac{B_1}{2\,!}\frac{x^5}{5}-\frac{B_2}{4\,!}\frac{x^7}{7}\ldots(-1)^{n-1}\frac{B_n}{(2n)\,!}\frac{x^{2n+3}}{2n+3}\ldots$$

Hence,
$$S_N=3Nk\left\{\frac{4}{3}-\frac{x}{2}+\frac{4B_1}{2!}\frac{x^2}{5}\,..+(-1)^{n-1}\frac{B_n}{(2n)!}\frac{4x^{2n}}{2n+3}\,..\right.$$
$$\left.-\log x+\frac{x}{2}-\frac{B_1}{2!}\frac{x^2}{2}\,..-(-1)^{n-1}\frac{B_n}{(2n)!}\frac{x^{2n}}{2n}\,..\right\}.$$

Thus the term in x disappears from the expansion, and in place of Ratnowsky's result we have

$$S_N=3Nk\left\{\frac{4}{3}-\log x+\frac{x^2}{40}\,..\right\},$$

or, approximately,

$$S_N=3Nk\left\{\frac{4}{3}-\log x\right\}.$$

§4. Assuming, with Ratnowsky, that the entropy of the liquid state can be calculated in the same way, and using accented letters for the liquid,

$$S'_N=3Nk\left\{\frac{4}{3}-\log x'\right\}.$$

The atomic heat of fusion, ρ, is equal to the difference of the entropies multiplied by the temperature of the melting point, T_s, or

$$\rho=T_s(S'_N-S_N).$$

Hence,
$$\rho=3NkT_s\log\frac{x}{x'}.$$

Introducing the characteristic temperatures, θ, θ' defined by

$$\theta=h\nu_m/k,\ \theta'=h\nu_m'/k,$$

$$\rho=3NkT_s\log\frac{\theta}{\theta'}.$$

§5. Ratnowsky, taking the values of the atomic heat of fusion determined experimentally, calculated the values of θ/θ' by his formula for a number of metals, and came to the conclusion that θ/θ' is approximately constant for these cases. I have recalculated the values of the ratio by the formula above for the metals considered in my first Paper, and all the results are collected for comparison in the table. It will be seen that the values of θ/θ' in the last column are far from constant, varying from about 1·38 in the case of the alkali metals, to 2·52 in the case of bismuth.

Values of θ/θ' for the Metals.

Metal.	Ratnowsky.	Allen.
Cæsium	—	1·371
Rubidium	1·29	1·376
Sodium	1·31	1·379
Potassium	1·30	1·381
Iron	—	1·415
Silver	1·32	1·417
Lead	1·33	1·421
Copper	1·36	1·454
Palladium	1·40	1·499
Aluminium	1·39	1·530
Mercury	1·42	1·583
Cadmium	1·47	1·635
Platinum	—	1·645
Zinc	1·48	1·657
Tin	—	1·872
Gallium	—	2·300
Bismuth	—	2·519

A further objection to the conclusion of Ratnowsky may be put forward from a consideration of the case of mercury. The value of θ for the solid state calculated by the formula of Lindemann is about 66°K. (Ratnowsky gives 61°K.). The value of θ' for the liquid state may be calculated if we assume that the theory of Debye may be applied, since the compressibility of liquid mercury is known. This gives $\theta'=205$°K., a temperature more than three times *higher* than that of the characteristic temperature of the solid state.

§6. It is to be noticed that the results tabulated by Ratnowsky for a number of chemical compounds in Tables II. to V. of his Paper are calculated by means of the formula

$$\rho = nNkT_S \log\frac{\theta}{\theta'},$$

which he regards as a rough approximation obtained by the omission of a term of the first order. Since it has been shown above that the terms of the first order disappear, his results in these cases may be regarded as accurate, and as showing an approximate constancy for the values of θ/θ', assuming suitable values are taken for n, the number of degrees of freedom of a molecule. Since the value of n is somewhat arbitrarily chosen so as to secure a constant result, no secure conclusion can be drawn from the cases cited.

ABSTRACT.

A criticism is given of a theory of the process of fusion recently put forward by Ratnowsky. The author of the theory obtains an expression on certain assumptions for the entropy of a substance in

the solid state. He then proceeds to deduce a simple formula suitable for use at high temperatures. It is shown that this formula is incorrect in consequence of the omission of a term in the expansion. Assuming, with Ratnowsky, that the entropy of the liquid state can be calculated in the same way as that of the solid, a corrected expression is deduced for the atomic heat of fusion which is equal to the difference between the entropies multiplied by the temperature of the melting point. Ratnowsky, taking the values of the atomic heat of fusion determined experimentally, calculated the ratio of the "characteristic temperatures" for a number of metals, and came to the conclusion that the ratio is approximately constant. The values have been recalculated by the corrected formula, and it is found that they are far from constant. The ratio calculated for mercury by an independent method does not agree with the conclusion of Ratnowsky.

XXXI. *Cohesion* (*Second Paper*). *By* HERBERT CHATLEY, *D.Sc.* (*Lond.*).

RECEIVED MARCH 24, 1916.

Introduction.

IT is very remarkable how little attention the subject of cohesion receives from students of physics. As far as the writer is aware, there is no standard text book which deals with the matter in any but the briefest way, and it is rarely that any suggestions are made which would link it with the theory of elasticity. The principal references in recent years are by Dewar (" Encyclopædia Britannica," art. " Liquid Gases "), Nernst (" Theory of the Solid State," London Univ. Press), and Pictet (" Les Basses Temperatures," Jnl. Roy. Soc. Arts, May 19, 1911). Curiously enough all three approach it from the same point of view—*i.e.*, low temperature phenomena. Dewar makes no suggestions as to rationale, beyond a tacit endorsement of Kelvin's gravitational theory ; Nernst identifies cohesive force with chemical affinity on the basis of the fact that Schonflies proved the possibility of building up crystals from the molecular lattices. Pictet adheres to his old hypothesis of ether atmospheres about the atoms, and regards cohesion as the gravitational effect of atom on atom, subject to the limitation imposed by the ether cushion, which is merely strongly attracted by the atom. Zenuer in the introduction to his " Technical Thermodynamics," abandons the Redtenbacher-Pictet theory, which he had previously adopted, but does not absolutely condemn it. Pictet distinguishes cohesion from chemical affinity, although asserting their specific unity, by supposing that the latter only operates (in a manner somewhat analogous to organic fertilisation of the ovum) when by thermal oscillations the propinquity of the material atomic centres is increased, the " ether atmosphere " which he postulates being burst through. In terms of the electron theory it may, perhaps, be supposed that elastic repulsion is due to the electrical repulsion between contiguous electron fields, but it is somewhat difficult to see how neutral atoms cohere under purely electrical conditions in virtue of electrical force only. Nevertheless, as mentioned below, cohesion seems to be comparable in magnitude with electrostatic force. To render the theory complete it is necessary to visualise an atom complex which :—

1. Attracts a dissimilarly charged atom with the full value corresponding to the charge and distance.

2. Attracts, when neutral, other neutral atoms with a force not incomparably small compared with electrostatic force. (A question here arises whether dissociated atoms do cohere in the strict sense of the word, or if they do not form molecules first.)

3. Attracts, neutral or charged, all other atoms, neutral or charged, with a force varying according to the Newtonian law at distances more than a few microns.

It would appear that molecular physics has or should have advanced to such a stage that this problem should not much longer remain unsolved.

Empirical Equations for Cohesive Force.

In a Paper read before the Physical Society in 1915 (Proc. Phys. Soc., Vol. XXVII., Pt. V., pp. 443-460, Aug. 15, 1915) the author suggested that certain empirical formulæ could be employed for the force between molecules known as cohesion. It is the object of this Paper to extend the subject and discuss various correlated facts and theories.

The principal formula suggested was as follows :—

$$\text{Cohesion} = \text{attraction} - \text{repulsion},$$

$$t = k_2 d^{-\gamma_2} - k_1 d^{-\gamma_1},$$

where t is the cohesive bond between two molecules, d is the distance between the centres of the molecules, k_1, k_2, γ_1, γ_2 are coefficients. k_1 and k_2 vary with the substance, k_1 (if not k_2 also) increases with temperature. All are functions of d, but within small limits may probably be regarded as constants.

The following special cases occur :—

1. *Normal Equilibrium* (*solid*)—

$t=0$, $k_2 d_0{}^{-\gamma_2} = k_1 d_0{}^{-\gamma_1}$. ($d_0$=normal molecular interval.)

2. *Elastic Strain of Small Amount*—

$\gamma_1 k_1 d_0{}^{-(\gamma_1+1)} - \gamma_2 k_2 d_0{}^{-(\gamma_2+1)} = E$. E is the modulus of elasticity in molecular terms (tension per molecule pair ÷ strain).

3. *Maximum Stress.*—

$$t_{\text{max.}} = k_2 (cd_0)^{-\gamma_2} - k_1 (cd_0)^{-\gamma_1},$$

or,

$$\gamma_1 k_1 c^{-\gamma_1} d_0{}^{-(\gamma_1+1)} - \gamma_2 k_2 c^{-\gamma_2} d_0{}^{-(\gamma_2+1)} = 0.$$

c=ratio of extension under maximum (stable) stress.

4. *Liquefaction*—

$$-a=k_2(c_1d_0)^{-\gamma_2}-mk_1(c_1d_0)^{-\gamma_1}.$$

a=atmospheric pressure per molecule pair in direction of bond, c_1=coefficient of expansion at temperature of liquefaction, m=ratio of coefficient k at this temperature to that at normal temperature.

5. *Pure Compression*—

$$-t=k_2d^{-\gamma_2}-k_1d^{-\gamma_1},$$

which must be negative, and equal to ∞ when $d=0$.

There are several difficulties in the way of evaluating the various coefficients in the above equations, but some useful values can be obtained by trial. Thus, if c is taken as 1·2, and $k_2=k_1$, $\gamma_2=4$, and $\gamma_1=5$, curves are obtained which closely resemble the stress-strain curves of metals. ($\gamma_1>\gamma_2$ necessarily. *V. loc. cit.*)

A further condition when d is at least $>2d_0$, and may be as much as $5d_0$, is that the only remaining force (in the absence of a specially induced electric charge) is that of gravity, so that then

$$t=k_2d^{-\gamma_2}=Gm_1m_2d^{-2},$$

the usual Newtonian rule, which makes $k_2=Gm_1m_2$ and $\gamma_2=2$.

Magnitude of the Attraction.

Kelvin opined that gravitation, as ordinarily understood, was competent to explain cohesive attractions. In the above-mentioned Paper the writer has examined this hypothesis, and finds it apparently incompatible with known molecular spacing.

Neglecting the repulsion (whose effect is, of course, to make the attraction less than it really is) a formula may be written

$$t=k_2d^{-\gamma_2}.$$

Taking the case of iron, and *assuming* that in a simple tension the cohesive strength is simply due to the bonds between molecular couples in the direction of the stress, we may write approximately

$$t=\frac{981f}{n^2}.$$

t=attraction per molecule pair in dynes.

f=total tension, grammes per square centimetre, say, 2×10^6, at ultimate stress.

n=molecules per centimetre length, say, 10^8.

Write $981=10^3$, $t=2\times10^{-7}$ dynes.

d is obviously $1/n$, say, 10^{-8} cm.

Then $\quad 2\times10^{-7}=k_2(10^{-8})^{-\gamma_2}=k_2 10^{8\gamma_2}$,

and $\quad k_2=2\times10^{-7-8\gamma_2}$.

If $\quad \gamma_2=2$, then $k_2=2\times10^{-23}$,

and using the Newtonian *form*,

$$k_2=G_2m_1m_2=G_2m^2,$$

where m is the mass per molecule. Let σ=specific gravity,

$$m=\frac{\sigma}{n^3}=\sigma d^3,\text{ and } m^2=\sigma^2d^6.$$

Writing for iron $\sigma=8$, and $d=10^{-8}$, as before,

$$G_2=\frac{k_2}{m_2}=\frac{2\times10^{-23}}{64\times10^{-48}}=3{\cdot}0\times10^{23}.$$

The ordinary molar value of G, the gravitation constant, is $6{\cdot}6\times10^{-8}$, so that

$$\frac{G_2}{G}=\frac{3\times10^{23}}{6{\cdot}6\times10^{-8}}\text{ approx. }0{\cdot}5\times10^{31},$$

i.e., at molecular distances the "gravitational" force is increased about 10^{30} *times.*

It is interesting to note that this ratio is about the same as that of the *electrostatic* and gravitational attractions of two atoms.

The charge on an electron being $3{\cdot}4\times10^{-10}$ electrostatic units, the repulsion between two electrons at 1 cm. apart is 10^{-19} dynes and between one iron atom (carrying one free electron) and another (lacking one electron) the force is presumably the same.

The gravitational attraction between two iron atoms at 1 cm. apart is

$$\frac{6{\cdot}6\times10^{-8}\times56^2}{10^{48}}=\text{approx. }2\times10^{-52}\text{ dynes,}$$

so that the ratio

$$\frac{\text{Electrostatic attraction}}{\text{Gravitational attraction}}=\frac{10^{-19}}{2\times10^{-52}}=0{\cdot}5\times10^{33}.$$

Considering the very rough character of these computations, the agreement is quite close, and seems to indicate that the force of cohesion is comparable with the electrostatic forces between atoms—*i.e.*, chemical affinity.

Nernst and Lindemann are of this opinion (Nernst, "Theory of the Solid State," p. 4), but allege other reasons.

The alternative method of expressing the space variation by varying γ_2 is, perhaps, more logical mathematically, but does not touch on the rationale of the process, unless some such hypothesis as Crehore's ("Electrical World," 1912) is adopted. In this case, as the author has shown (*loc. cit.*, p. 448), a value $\gamma_2=6$ nearly fits the circumstances.

The Nature of Cohesive Force.

There is a general agreement that cohesive force is inferior in intensity to chemical affinity. The formulæ given above indicate a ratio

$$\frac{0\cdot5\times10^{31}}{0\cdot5\times10^{33}}\doteq10^{-2},$$

but there is, of course, no accuracy in a result obtained by such approximate methods.

Very great pressure even up to the elastic limit does not bring two smooth steel surfaces into such close contact that they cohere. This may, perhaps, be due to the presence of a film of air, and it would be interesting to find what degree of cohesion, over and above that due to air pressure, could be produced with surfaces of different degrees of smoothness pressed together *in a vacuum.*

When in a plastic (semi-liquid) condition, materials cohere under small pressure. An analogous fact is the smaller amount of tensile strength under such conditions. Lindemann believes that liquefaction occurs when the amplitude of the molecular oscillations is about the same as the molecular interval. If so, in a partially liquid substance, many of the surface molecules rise and fall to a relatively great extent, and presumably two plastic surfaces brought together cohere by reason of the very close proximity of the molecules during their ascents from the respective surfaces.

(An interesting and possibly useful speculation arising out of Lindemann's hypothesis is that dissociation occurs when the molecular frequency synchronises with the atomic frequency.)

The range of cohesion is very small (as has been shown experimentally by Quincke), since the force diminishes from great (tensile) values in solid to very small ones * in liquids with only small change of volume, and becomes less than zero in gases even under such great pressure that the volume is comparable (say, 10 times greater) with that of the liquid. The deviations from Boyle's law at high pressures, apart from Van der Waal's correction for the volume of the molecules, may perhaps have some cohesive relation, but the effect, if any, is excessively minute.

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* Really negative ones, since the liquid is only maintained by air pressure.

The average liquid occupies only a slightly larger volume than the solid from which it is produced, so that a very minute increase in the molecular interval causes an enormous reduction in the cohesive force. It must not, however, be forgotten that this is partially due to a great increase in the repulsive factor, but the fact of fracture in solids without very great extension indicates the simultaneous decrease of the attraction. The cases of ice and iron which contract during liquefaction may perhaps be due to chemical change. Ice, for instance, is believed to have the formula $2(H_2O)$ (Nernst, "Solid State," p. 91), whereas water *may* be H_2O. If so, the more complex molecule probably has a smaller density, so that we may *suppose* that at the critical temperature of maximum density "liquid ice" becomes "water," or that from the commencement of liquefaction to 4°C. there is a gradual change in the proportions of ice and water. Presumably such a chemical change would have some distinct thermal or electrical effect.

Cohesion can be effective in any direction about a particle, since amorphous solids exist, but the fact of crystallisation shows that it has directional variation—*i.e.*, it is a vector quantity. Chemical affinity is obviously a vector quantity as stereotomy shows, but the angular rate of change of the force must be immensely greater in the case of chemical attraction, since no amount of internal friction seems able to resist the formation of the atomic lattices termed molecules. Presumably the enormous electrostatic forces which exist around free atoms are not wholly neutralised in the formation of molecules, and cohesion is due to what electricians call "stray field."

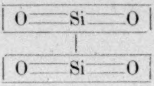
If each atom be envisaged as a charged sphere enveloped in a dielectric (like Redtenbacher and Pictet's "Ether Atmospheres," which correspond to Thomson's electron fields about the positive core), then groups of such can be conceived, charged in various combinations, forming stable geometrical systems (the molecules). Such systems roughly aggregated would cohere by reason of stray field (amorphous solids), or if allowed to form slowly under conditions of maximum freedom would establish configurations of maximum stability (crystals). There is a strong suggestion of the "three body" problem of astronomy in a still more complex form.

The outstanding difference between chemical affinity and cohesion lies in the selective character of the first. As far as the valency bonds of an atom being able to hold a molecule is concerned this is a common feature in organic compounds. What is distinct in the selective process is the feature of "saturation." Consider the case of silica $(SiO_2)_2$.

1. In each sub-molecule, the four valency bonds of the silicon atom are linked in pairs to two oxygen atoms, according to the stereotomic formula. This is purely chemical.

$$\boxed{O = Si = O}$$

2. The sub-molecules are linked in pairs, if Nernst's formula $(SiO_2)_2$ is correct, thus :—



$$\begin{array}{c}\boxed{O = Si = O}\\ |\\ \boxed{O = Si = O}\end{array}$$

This is chemical in so far as it occurs in constant proportions, but is cohesive in so far as it is the linkage of molecules as distinct from atoms.

3. The silica molecules are linked to one another irrespective of quantity, but with a configuration of maximum stability (crystal) with four axes (hexagonal system). Linkage can occur without geometrical form (amorphous solid). The magnitude of the linkage forces is inferior to that of (1) and (2), but not incomparable (cohesion).

4. If gravitation is not a particular case of cohesion, then, in addition there is a small mutual attraction with no vector quality in accordance with Newton's law.

There is probably some relation between the number of atoms per molecule, and the system of crystallisation. Thus, $(H_2O)_2$ and $(SiO_2)_2$ both contain 6 (or 3) atoms per molecule, and crystallise according to a hexagonal system.

Schonflies claims to have proved the possibility of building crystals up from molecules in an analogous manner.

It would seem possible to deduce from the fields about different stable systems of differently charged spheres some idea as to the feasibility or otherwise of explaining cohesion on these lines.

Relation of Frequency to Temperature in a Solid.

From formula in "Cohesion" (p. 444).

$$f=\frac{\sqrt{Js\theta}}{\pi\Delta}.$$

Write $\Delta=\Delta_0[1+m\theta]$.

Δ_0=molecular interval at abs. zero.

$$f=\frac{\sqrt{Js\theta}}{\pi\Delta_0[1+m\theta]};\ J=4{\cdot}2\times10^7.$$

Example—

Iron: $s=0{\cdot}11$,

$$f=\frac{684{\cdot}1\sqrt{\theta}}{\Delta_0[1+m\theta]}.$$

If $\theta=900°$C. abs.

$$f=\frac{20523}{\Delta_0 1+0{\cdot}01]}.$$

Taking $\Delta_0=10^{-8}$,

$f=2{\cdot}0\times10^{12}$ at 900°C. abs.

and $0{\cdot}5\times10^{12}$ at 450°C. abs.

or, *if* $f=4{\cdot}0\times10^{14}$ at 900°C. abs. (*See* "Cohesion," p. 445.)

$$\Delta_0=0{\cdot}5\times10^{-10}.$$

(*Note.*—Clerical error on p. 445, $0{\cdot}5\times10^{-8}$ should be $0{\cdot}5\times10^{-10}$. Either the radiation frequency exceeds the molecular frequency as calculated above or the molecular interval is much less.)

Generally, if $\Delta_0=10^{-8}$,

$$f=\frac{684\sqrt{\theta}}{10^{-8}[1+m\theta]}=\text{say, }7\times10^{10}\sqrt{\theta}.$$

Cf. Lindemann's formula (Nernst, p. 49) for *atomic* frequency.

$f=3{\cdot}08\times10^{12}\sqrt{\frac{Ts}{mv^{2/3}}}$=from 1 to 50 times 10^{12} for most monatomic solids (for *monatomic* solids), where T_s is melting temperature, v is vol. in cubic centimetres of m grammes, m is atomic weight.

DISCUSSION.

Dr. H. S. **Allen** (communicated): The nature of the attractive force producing cohesion and rigidity has been discussed by several writers, including Sutherland,* who attributes the attraction to electrostatic forces arising from electric doublets, and A. P. Mathews.† The latter writer suggests that molecular cohesion may be due to magnetic forces. "Is it not possible that molecular cohesion, involving, as it does, both atomic and valence electrons (atomic weight and valence), is due, perhaps, to the magnetic effects produced by the movements of these electron couples? In this view the atoms would be united by their electrostatic affinities, and these same valences and the other atomic electrons by their magnetic effects produce the molecular cohesion." The difficulty attaching to this view appears to be the necessity for postulating very large magnetic moments for the molecules. "Weiss, who has considered the possibility of the identity of cohesion and magnetism, states that he will shortly show that they cannot be identical." It must be emphasised that in a crystalline solid, very intense *local* molecular fields must exist whatever may prove to be the nature of the cohesive forces. An interesting illustration of quasi-rigidity imparted to an assemblage of independent bodies by the application of a magnetic field, is afforded by a handful of small iron nails or tacks thrown between the poles of a strong electromagnet. The nails arrange themselves in chains or bridges between the poles, such chains offering considerable resistance to distortion. If the nails are sufficiently numerous they form a compact mass between the magnet poles which can be broken only by the application of a large force. In such a case the *local* forces predominate. This has been emphasised by Larmor‡ and by Oxley.§ "If we suspend a bunch of iron nails from the pole of a magnet, we find that they adhere to each other endwise, and repel one another sideways, while non-adjacent nails have no action on one another." Thus modifications in the values of the forces are necessitated "by the recognition of the discrete or molecular character of the polarised elements." Amorphous solids may be regarded as supercooled liquids. Even in a liquid the force of cohesion may be considerable, as is shown by the comparatively large value the tensile stress may attain. The important point in Prof. Chatley's Papers appears to be the clear recognition of the fact that it is necessary to consider both an attractive and a repulsive force between the molecules. It may be mentioned that in 1903 Mie‖ advanced a theory of monatomic solid bodies characterised by the assumption that the atoms are constrained in definite equilibrium positions by attractive and repulsive forces between them. The same hypothesis was afterwards employed by Grüneisen¶ and by Ratnowsky** in the development of an equation of state for solid bodies.

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* *See* especially "The Electric Origin of Rigidity," "Phil. Mag.," Vol. VII., p. 417, 1904.

† "Journal" of Physical Chemistry, Vol. XVII., p. 481, 1913.

‡ Larmor, "Proc." Roy. Soc., A, Vol. LII., p. 64, 1892.

§ Oxley, "Phil. Trans." Roy. Soc., A, Vol. CCXV., p. 91, 1914.

‖ "Ann. d. Phys.," Vol. XI., p. 657, 1903.

¶ "Physik. Zeitschr.," Vol. XII., p. 1023, 1911.

** "Ann. d. Phys.," Vol. XXXVIII. p. 637, 1912.

XXXII. *On the Significance of Ionic Migration Experiments.* *By* DR. S. W. J. SMITH, F.R.S.

RECEIVED JULY 18, 1916.

1. *Migration Data for Copper Sulphate Solutions.*—The results presented in the Paper read recently before the Physical Society by Mrs. C. H. Griffiths* are such that, as I pointed out at the time,† they are not likely to be accepted without question by those who have been accustomed to regard Hittorf's fundamental measurements, of the migration constant for copper sulphate, as certainly correct " within one or two units in the second decimal place."

The values obtained for this constant by Mrs. Griffiths are uniformly higher than those of Hittorf. For the concentrated solutions the difference is relatively small. It is not much greater than the amount by which Hittorf's results may be in error. The difference increases with dilution until it amounts to four or five units in the second place, and there is no sign that it would not have become greater still if the dilution had been carried as far as it was by Hittorf.

For well-known reasons, the properties of dilute solutions have been the subject of careful study and the migration constant of such solutions has not escaped attention. The experiments upon which the greatest reliance has been placed—*e.g.*, those of Bein‡—have tended to confirm the substantial correctness of Hittorf's numbers in this region. The experiments of Kirmis, as he himself remarked,§ seemed to show that, for concentrated and for dilute solutions alike, the results are not seriously in error. The experiments of Metelka are not exactly comparable with those of Hittorf; but, except in one solution, they agree with his. The same is true of some of Wiedemann's results and also of isolated experiments by Gordon‖ and by Hopfgartner,¶ within the limits already mentioned. The difference between Hittorf's results and those obtained by Mrs. Griffiths is the more striking in that the appa-

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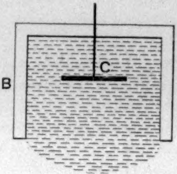
[*] " Proc." Phys. Soc., 28, p. 132, 1916.
[†] " Bulletin " Phys. Soc., 1916, p. 24.
[‡] " Wied. Ann.," 46, p. 29, 1892; " Zeits. Physik. Chem.," 27, p. 1, 1898.
[§] " Wied. Ann.," 4, p. 507, 1878.
[‖] " Zeits. f. Physik. Chem.," 23, p. 469, 1897.
[¶] *Ibid*, Vol. 25, p. 115.

ratus used by her resembles the original apparatus * more closely in some ways than any of the various devices which have been used to test or to improve upon Hittorf's measurements. In both the cathode vessel is a vertical cylinder closed at the top, and the measurements depend, in closely related ways, upon what happens within this vessel during the course of the experiment.

2. *Two Methods of Applying Hittorf's Principle.*—The relation between the two methods may be expressed in the following way, neglecting at first certain necessary qualifications which will be considered afterwards.

Imagine a solution of copper sulphate, from which copper can be deposited upon a cathode, C, to be contained within a cathode vessel B, as shown diagrammatically in the Figure below.



Let the weights of the Cu and SO_4 ions (in gms.) be represented by c and a respectively, and let u/v represent the ratio of the velocities of these ions under the same potential gradient. Then, during the deposition of $(u+v)c$ gms. of Cu upon C, $v(a+c)$ gms. of Cu SO_4 will leave the liquid round the cathode, va gms. SO_4 will leave the cathode vessel and uc gms. Cu will enter it.

If we denote the loss in weight of the cathode vessel by l, the loss of Cu SO_4 by l' and the weight of copper deposited by w, we find at once that—

$$\frac{l'}{w}=\frac{v}{u+v}\cdot\frac{a+c}{c}=\frac{l}{w}+1.$$

And if we write $v/(u+v)=n$,

we get $$n=\frac{c}{a+c}\cdot\frac{l'}{w}=\frac{c}{a+c}\cdot\left(\frac{l}{w}+1\right).$$

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* "Pogg. Ann.," 89, p. 187, 1853.

Hence, if we measure either l'/w or l/w we can determine n, the value of $c/(a+c)$ being equal to 1/2·511, very nearly, when modern atomic weights are used.

Hittorf measured l' directly (being able to isolate the cathode vessel for this purpose), while Mrs. Griffiths has measured l.* Hittorf, for reasons which he gives, deduced the values of w from the weights of silver deposited in a voltameter in series with the migration vessel; but, except for the weaker solutions, he also measured w directly—the copper being deposited upon a (silver) cathode of a shape to which reference is made later on. The values of w, obtained directly and indirectly, were usually the same within a few parts per thousand. Mrs. Griffiths deduces the value of w from the current, the time it is passed and the electrochemical equivalent of copper.

The fact that Mrs. Griffiths, in addition, measured the current density and hence, knowing the concentration of the solution, the electrochemical equivalent of copper and its atomic weight, calculated u and v separately (really au and av, where a is the coefficient of ionisation) does not constitute an essential difference between the methods. The value of $a(u_0+v_0)$ can be calculated for any solution of which the conductivity and molecular concentration are known and hence, from measurements by Hittorf's method, the separate values of au_0 and av_0 can be determined. Here u_0 and v_0 refer to the ionic velocities under unit potential gradient. The values of au and av given by Mrs. Griffiths correspond with undetermined potential gradients, since the conductivities of the solutions employed were not obtained. Similar calculations could, if desired, be made from Hittorf's data, since he also gives the diameter of his cathode vessel; but, as a matter of fact, the validity of this method of measuring ionic velocities is now doubtful because, if the ions are hydrated, as seems to be the case in general, the migration constant n can only accidentally be equal to $v/(u+v)$ in solutions of moderate concentration.

3. *Disturbing Factors.*—Before proceeding further it is necessary to remove the imperfections from the sketch, given above, of the two different methods of applying Hittorf's principle.

There are at least two disturbing factors, recognised by Mrs. Griffiths, of which Hittorf was fully aware.† In the first place the copper deposited on the cathode reduces the volume of the cathode vessel and so tends to expel some of the solution. In the second, the disappearance of Cu SO_4 from the cathode region is accompanied by a decrease in the volume of the solution from which it is removed. This tends to cause some of the surrounding liquid to enter the cathode vessel. The volume of liquid which the deposited copper tends to expel is obviously w/d, where d is the density of the copper deposited under the conditions of the experiment (to which Hittorf ascribes the value 8·914 obtained by Marchand and Scheerer). To set against this we have the volume which tends to enter and which, as Hittorf points out, it is impossible to estimate exactly. The reason for this is that we do not know exactly how the loss of salt is, as it were, distributed over the water which remains.

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* By suspending the cathode vessel from the pan of a balance.

† *L.c.*, p. 197.

Suppose the original solution to be of density ρ, and to contain β gms. of Cu SO_4 per unit weight. (Hittorf gives both of these quantities for the solutions which he used.) Suppose further that the loss of salt, l', is distributed over a certain mass, W, of the water above the cathode and let this water (at the end of the experiment) give with the Cu SO_4 which it contains a solution of density ρ' containing β' gms. Cu SO_4 per unit weight. The initial volume of this solution was $W/\rho(1-\beta)$. The final volume is $W/\rho'(1-\beta')$. The contraction is, therefore,

$$W\{1/\rho(1-\beta)-1/\rho'(1-\beta')\}.$$

We have also $$l'=W\{\beta/(1-\beta)-\beta'/(1-\beta')\}.$$

Whence the contraction is—

$$l' \cdot \frac{1/\rho(1-\beta)-1/\rho'(1-\beta')}{\beta/(1-\beta)-\beta'(1-\beta')}.$$

The values of ρ and β are determined by the concentration of the solution used in the experiment, but the values of ρ' and β', for a given value of l', depend upon the assumed magnitude of W. The maximum value of W is obviously the whole mass of water round and above the cathode in the cathode vessel. In that case the values of ρ' and β' will also be the largest possible for a given value of l'. It happens at the same time, for most solutions of Cu SO_4 at any rate, that the contraction for a given loss of salt will be greatest when the loss is distributed as uniformly as possible over the whole of the water above the cathode.

If, on the other hand, the loss is restricted as much as possible in its distribution, for example so that a certain mass of water is deprived of the whole of its salt content while the rest contains the original percentage of salt, then the change in volume for a given loss of salt will be relatively small. Its value will be $l'\{1-\rho(1-\beta)\}/\beta\rho$.

4 *Their Influence in Hittorf's Method.*—The actual contraction in any given case will be somewhere between these two extremes, being nearer the one or the other according as the mixing of the different elements of the cathode solution is more or less complete.

It will be sufficient for the moment to assume that the contraction can be represented by $l'\delta$. The net amount of $\mathrm{Cu\,SO_4}$ lost by the cathode vessel during the experiment, in consequence of the two disturbing factors, will then be—

$$\left\{\frac{w}{d}-\frac{a+c}{c}nw\delta\right\}\beta\rho.$$

Hence the corrected expression for l', the total loss of $\mathrm{Cu\,SO_4}$ by the cathode vessel during the experiment, is—

$$l'=w\left\{n\,.\,\frac{a+c}{c}(1-\beta\delta\rho)+\frac{\beta\rho}{d}\right\},$$

whence

$$n=\frac{c}{a+c}\,.\,\frac{l'/w-\beta\rho/d}{1-\beta\delta\rho}\,.\quad\quad\text{(H.)}$$

If we write this equation in the form

$$n=\frac{c}{a+c}\,.\,\frac{l'}{w}\,.\left\{1-\frac{\beta\rho(w/l'd-\delta)}{1-\beta\delta\rho}\right\},$$

we see at once that the simple theory of Hittorf's method will lead to appreciable error unless either

(i.) $$w/l'd-\delta=0$$

or (ii.) $$\frac{\beta\rho(w/l'd-\delta)}{1-\beta\delta\rho}$$

is small in comparison with unity.

5. *Estimation of Possible Errors.*—With respect to (i.) above, it happens, curiously enough, that, in dilute solutions of $\mathrm{Cu\,SO_4}$, $w/l'd$ can be greater than δ, while in concentrated solutions the converse is true. Hence, subject to the limitations imposed by uncertainty in the value of δ in any particular case, there should be solutions for which the simple theory is almost

exactly sufficient. Such solutions are those of which the density lies somewhere near 1·05.* In more dilute solutions the uncorrected n would be too large, in more concentrated solutions too small.

The condition (ii.) is, however, of more general interest. From what has just been said, it will be seen that, in order to discover the maximum error in n, caused by neglect of volume changes, it is enough to consider the case of the most concentrated solution used. For, on account of the factor β, the quantity $\beta\rho(w/l'd-\delta)/(1-\beta\delta\rho)$ will always be much smaller in very dilute than in concentrated solutions.

The strongest solution used by Hittorf had a density of about 1·15 ($\beta=0{\cdot}136$). For this the value of $w/l'd$ was approximately 0·06 and that of $\beta\rho$ approximately 0·16. Hence we may put

$$n=n'\{1-0{\cdot}16(0{\cdot}06-\delta)\},$$

where n' is the uncorrected value of n. In order to estimate δ, Hittorf assumed that the cathode loss could be considered to result in the substitution, for a certain quantity of the original solution, of a quantity, containing the same amount of water, of the second solution which he used. He knew the values of ρ' (about 1·10) and β' (about 0·095) for this solution and hence deduced a value for δ. It was approximately 0·07. In that case, we should have $n=n'\times 1{\cdot}0016$, or the uncorrected value of n would be about 1·5 parts per 1,000 too small. Since the unavoidable errors of experiment were greater than this, Hittorf concluded that the correction was superfluous.

If Hittorf had assumed the loss to consist in the removal of the whole of the salt from a given mass of the solution, leaving the rest unchanged, the value of δ would have been approximately 0·03. In this extreme case (against which diffusion would operate effectually) n' would be too large, but would still be within 0·5 per cent. of the true value.

If, on the other hand, we make use of the tables compiled by Gerlach† from data given earlier by Schiff‡ (as, apparently, Mrs. Griffiths has done), we can estimate the limiting value of δ in the other direction, *i.e.*, when we suppose the loss shared equally by the whole of the liquid above the cathode. The value of δ would then be about 0·11 and, in this case, n' would be about 0·8 per cent. too small. Such a correction would bring Hittorf's higher values considerably nearer to those of Mrs. Griffiths.

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* Assuming the values of δ given by Mrs. Griffiths to be approximately correct.

† "Zeits. Analyt. Chem.," 8, p. 288, 1869.

‡ "Ann. Chem. Pharm.," 110, p. 71, 1859.

When estimating the reliability of Hittorf's results, it must not be forgotten, however, that in later experiments[*] the disturbing factors here considered were avoided.

The calculation of the cathode loss was not based upon the volume of the liquid contained by the cathode vessel after the experiment, but upon its weight. Thus, let w_1 be the weight of the solution in the cathode vessel after the experiment and w_2 the weight of Cu SO$_4$ (determined by analysis) which this solution contains. Then, if β be the weight of salt per unit weight of the original solution, the true cathode loss of salt is expressed by $l' = \beta(w_1 - w_2)/(1-\beta) - w_2$, and the simple formula

$$n = \frac{c}{a+c} \cdot \frac{l'}{w} \text{ applies.}$$

The same expression holds good, with sign reversed, for the anode gain. The result obtained for the solution of specific gravity about 1·10, by this method, using the anode gain, was (as it should be) slightly larger than, but practically identical with, that previously obtained—viz., 0·716, compared with 0·713.[†]

6. *The Griffiths Method.*—In this method of measuring the migration constant, the loss of weight of the cathode vessel owing to migration is $\frac{a+c}{c} nw - w$. The loss due to the disturbing influences considered above is now

$$\left\{ \frac{w}{d} - \frac{a+c}{c} nw\delta \right\} \rho.$$

Hence the correct value for n, if l is the total loss in weight of the cathode vessel, is

$$n = \frac{c}{a+c} \cdot \frac{l/w + 1 - \rho/d}{1 - \delta\rho}. \quad . \quad . \quad . \quad . \quad . \quad \text{(G.)}$$

If we write this in the form

$$n = \frac{c}{a+c} \cdot \left(\frac{l}{w} + 1 \right) \left\{ 1 - \frac{\rho(w/(l+w)d - \delta)}{1 - \delta\rho} \right\},$$

---

[*] " Pogg. Ann.," 98, p. 1, 1856.

[†] All Hittorf's results would be altered slightly by the substitution of modern atomic weights for those used by him.

we see that the simple theory of the method will lead to appreciable error, as in the other case, unless

either (iii.) $w/(l+w)d-\delta=0$

or (iv.) $$\frac{\rho(w/(l+w)d-\delta)}{1-\delta\rho}$$

is small in comparison with unity.

7. *Its Disadvantages Compared with Hittorf's Method.*—With respect to (iii.), as in the case of (i.), it will be found that the condition can apparently be satisfied when ρ is in the neighbourhood of 1·05. But comparing (iv.) with (ii.), it will be seen that the correction no longer decreases rapidly as the solutions become more and more dilute, and, even in the strongest solutions, is much greater than before. It follows that if there is any uncertainty as to the volume changes, already discussed, the second method will compare unfavourably with the first.

8. *Uncertainty in the Estimates of* δ.—The following numerical example will illustrate the uncertainty with respect to δ.

For the solution of density 1·0273, Mrs. Griffiths takes $\delta=0{\cdot}044(31)$, which is deducible from Gerlach's values,

$$\rho=1{\cdot}1038,\ \beta=0{\cdot}03834$$
$$\rho'=1{\cdot}0254,\ \beta'=0{\cdot}02556,$$

and obtains for n the value 0·6910, Hittorf's value for a similar solution lying between 0·645 and 0·65.

Inspection of Gerlach's data seems to show that they are not as accurate as Mrs. Griffiths supposes. Apart from this, there is the difficulty that the data given by Hittorf* (so far as they are comparable), by Kohlrausch† and by Archibald‡ lead to other values for δ. The results are not very consistent with one another, but tend to show that the value $\delta=0{\cdot}04$ is too high. Perhaps as much as 50 per cent. too high. Hence, even when the method of allowing for volume changes which Mrs. Griffiths adopts is assumed to be correct, the uncertainty of the data upon which she relies is such that the value of n to which her own observations lead may be considerably less than 0·69.

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* *L.c.*, p. 196, 1853.

† "Wied. Ann.," 6, p. 20, 1879.

‡ "Trans." Nov. Scot. Inst., Vol. IX., 1897, quoted in "Landolt-Börnstein-Roth Tabellen," 4 Aufl., p. 284, 1912.

9. *Uncertainty Concerning the Effective Density of the Cathode Deposit.*—The doubt concerning δ is not the only one. The value $d=8{\cdot}952$, also taken from tables by Mrs. Griffiths, may be sufficiently near the true density of electrolytically deposited copper under normal circumstances; but there is always the danger that the amount of solution which the electrolytic processes tend to expel from the cathode vessel is greater than w/d. Small quantities of gas, such as hydrogen deposited with the copper, oxygen freed from solution by change in temperature or evolved at the anode, may collect in the cathode vessel. The effect of these will be practically equivalent to a reduction in d since their weight will be negligible. Hydrogen is the most probable source of error of this kind. It would tend to make the calculated value of n too large and, since it is most likely to be evolved from the weakest solutions, it is a possible cause of the main difference between the results obtained by the two methods. For, as in the case of δ, the first method is obviously affected much less than the second by changes in d.

It is interesting in this connection to recall the remarks made by Hittorf with respect to the shape which he chose for his cathode.* It consisted of a silver cone with axis vertical and apex downwards. A horizontal glass disc was fixed at its centre to the apex of this cone in order, as he explains, to obtain a nearly uniform deposit. The anode was a horizontal, perforated, disc; but, referring to the cathode, Hittorf says that if the latter is a horizontal plate the deposited metal is not adherent. He remarks also † that in dilute solutions (of density 1·025 or less) the copper was deposited, even on his cathode, in a spongy form and could not be weighed. A spongy deposit is a frequent precursor of hydrogen.

Mrs. Griffiths obtained a value for the electrochemical equivalent of copper, which was not more than one-third per cent. too small, by means of a cathode similar to that employed in the migration experiments. It might be inferred from this that the effect of hydrogen in the migration experiments was probably unimportant. It has to be remembered however, that, in the determination of the equivalent, the cathode was not enclosed. Apart from the fact that hydrogen which escaped would not materially affect the result in this case, it is obvious that efficient convection, which is all-important if evolution of hydrogen is to be prevented, would be more likely to occur in this than in the migration experiment.

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* *L.c.*, p. 187.

† *L.c.*, p. 195.

To sum up, we may say that the results obtained by the second method, ingenious as it is, cannot be accepted as superior to Hittorf's until it is shown that errors in the estimation of δ and of d, which can easily occur, have been avoided.

10. *Hydration and its Influence upon the Results obtained by the Two Methods.*—The possibility that the ions may be hydrated has already been mentioned; but has, so far, been ignored. It remains to enquire how this hydration would affect the significance of the results obtained by either method.

For this purpose we may suppose that the gm. ions of Cu and SO_4 carry with them, respectively, C and A gm. mols. of water. With this supposition we see that when $(u+v)c$ gms. of Cu are deposited, u gm. ions of Cu give up uC gm. mols. of water at the cathode, while v gm. ions of SO_4 carry vA gm. mols. away.

If, for definiteness, we assume $uC>vA$, it follows that $\frac{uC-vA}{(u+v)c}w$ gm. mols. of water are carried into the cathode space, for every w gms. of Cu deposited.

There is thus another possible source of dilution at the cathode. It will tend to increase the amount of solution expelled from the cathode vessel.

We may consider this effect to be superposed on that already dealt with. We shall then have to find how the volume of a solution containing a given mass M of salt is increased when the amount of water W, which it contains, is increased by a known quantity. Using the same symbols as before, we write

$$V=\frac{M}{\beta\rho} \text{ and } W=\frac{1-\beta}{\beta}M,$$

whence

$$\left(\frac{\partial V}{\partial W}\right)_M=\partial\left(\frac{1}{\beta\rho}\right)\Big/\,\partial\left(\frac{1-\beta}{\beta}\right).$$

Following the previous plan we may write this in the form

$$\gamma=\frac{1/\beta\rho-1/\beta'\rho'}{(1-\beta)/\beta-(1-\beta')/\beta'},$$

from which the value of γ for a solution of given density ρ can be found in the same way and with the same limitations as was δ.*

Hence, if we denote the weight of a gm. mol. of water by g, the amount by which the volume of the cathode liquid is increased, when w gms. of Cu are deposited, is

$$\frac{uC-vA}{(u+v)c}wg\gamma,$$

and the complete expression for the volume of $Cu\,SO_4$ solution expelled from the cathode vessel should be

$$\left\{\frac{w}{d}+\frac{uC-vA}{(u+v)c}gw\gamma-\frac{a+c}{c}nw\delta\right\}.$$

Hence the total loss of $Cu\,SO_4$ by the cathode vessel is $\frac{a+c}{c}nw$ plus the above quantity multiplied by $\beta\rho$.

Writing out the new expression for l', and comparing it with that already found, it will be seen that we can deduce the equation

$$n=\frac{v}{u+v}=n_H-\frac{g}{a+c}\cdot\frac{\beta\gamma\rho}{1-\beta\delta\rho}\cdot\{(1-n)C-nA\},$$

where n_H is the value for n found by Hittorf's method when hydration is ignored.

Considering the plan adopted in the second method in the same way, it will be seen that the total loss in weight of the cathode vessel, owing to migration, is

$$\left\{\frac{a+c}{c}nw-w\right\}-\frac{g}{c}\{(1-n)C-nA\}w,$$

while the amount of solution expelled owing to volume changes produced within the cathode region, is the same as in the first case.

Writing down the new expression for l, we can deduce the result

$$n=\frac{v}{u+v}=n_G-\frac{g}{a+c}\cdot\frac{\gamma\rho-1}{1-\delta\rho}\cdot\{(1-n)C-nA\},$$

where n_G is the value for n found by the Griffiths method when hydration is neglected.

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* The corresponding equation for δ, obtained from $V=\frac{W}{\rho(1-\beta)}$ and $M=\frac{\beta}{1-\beta}W$, is $\left(\frac{V}{\partial M}\right)_W=\partial\left(\frac{1}{\rho(1-\beta)}\right)\Big/\partial\left(\frac{\beta}{1-\beta}\right)$.

When this expression is compared with that containing n_H, it will be seen that the experimental values, n_G and n_H, will not coincide unless the values of

$$\frac{\beta\gamma\rho}{1-\beta\delta\rho} \text{ and } \frac{\gamma\rho-1}{1-\delta\rho}$$

are the same within the limits of experimental error.

The values of these quantities, for different values of ρ, can be determined if we assume Gerlach's tables to be sufficiently accurate. The following approximate table will serve to indicate how they vary with ρ :—

ρ.	$\beta\gamma\rho/(1-\beta\delta\rho)$	$(\gamma\rho-1)/(1-\delta\rho)$
1·1083	0·116	0·115
1·0554	0·058	0·057
1·0273	0·028	0·028

They are thus practically identical when ρ is small, although, as ρ increases, the numbers in the second column increase rather more rapidly than those in the third. This means that n_H should increase slightly with respect to n_G as ρ increases. The actual difference for any value of ρ would be negligible unless the factor $\{(1-n)C-nA\}$ were large since $g/(a+c)$ is only 0·113. But, in any case, it is seen that hydration cannot be the cause of the difference between the results obtained by the two methods.

11. *The Variation in the Value of the Migration Constant.*—The data just given would enable us to calculate the true value of n from a series of values of the migration constant, using solutions of different strengths, if we could assume that the ratio of the ionic velocities and the degree of hydration of the ions were constant.

If, to test the validity of such assumptions, we take Mrs. Griffiths' values of n_G, we find that they appear to be fairly consistent with $n=0{\cdot}675$. Similarly if, from Hittorf's measurements, we obtain corresponding values of n_H, we find that the value of n, which would satisfy Hittorf's results, would be approximately 0·625. This is Metelka's value for the migration constant in very dilute solutions, and, since in such solutions n_H and n should practically coincide, it might seem that u/v is, in fact, independent of the concentration, and that the degree of hydration of the ions is also constant.

This simple interpretation of the results does not, however, agree with data obtained by Steele[*] using the moving boundary method of comparing ionic velocities. For a solution containing 1 gm. mol. of $Cu\,SO_4$ per litre he found $v/u=2{\cdot}71$, whence $n=0{\cdot}73$; while for a solution of half this strength he found $v/u=1{\cdot}94$ or $n=0{\cdot}66$. Therefore, if these results are correct, n is far from constant in the region of concentration to which they apply. Variations of this kind would complicate the theory of the experiments. Their most probable cause would be variations in C and in A. If, for simplicity, we assume the moving particles to be spherical, and to have volumes proportional to C and to A, an attempt to interpret the results can be made; but it would appear not to meet the present case. With dilute solutions, however, such hypotheses are apparently more successful[†], and attempts have been made to deduce values of C and A in this region in which, probably, their variations are comparatively small.

12. *Comparisons of* n_H *with* $n=v/(u+v)$.—It would appear that dilute solutions of $Cu\,SO_4$ have not been examined by the direct method[‡]; but results have been published for other salts. In some of these the migration constant obtained by the Hittorf method is practically identical with the value of $v/(u+v)$ obtained directly. For example,[§] in dilute NaCl, $n=u/(u+v)=0{\cdot}617=n_H$.

The disturbing influence of hydration would, as the equations of §10 show, be relatively unimportant in dilute solutions. In more concentrated solutions, however, the value of

$$\frac{g}{a+c}\cdot\frac{\beta\gamma\rho}{1-\beta\delta\rho}\cdot\{(1-n)C-nA\}$$

might easily become appreciable. For a normal solution of Na Cl, Denison and Steele found $n=u/(u+v)=0{\cdot}614$, while the Hittorf method had given $n_H=0{\cdot}637$. The existence of such differences was verified repeatedly. It was not seen till later that they could be due to hydration. The most satisfactory evidence was supplied by Washburn.[||]

His method[¶] can be presented in the following way: Suppose that a substance can be found which, when dissolved along with the electrolyte, does not move under the influence of the potential gradient. Let the solution contain this substance in known amount, say, r gms. per cc. During the deposition of w gms. of metal, the volume of the solution expelled from the cathode vessel will be, as before,

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[*] Phil. "Trans.," A., 198, p. 129, 1902.

[†] *Cf.* Riesenfeld and Reinhold, "Zeits. Physik. Chem.," 66, p. 682, 1909.

[‡] *Cf.* Steele, *l.c.*, p. 122.

[§] Denison and Steele, "Zeits. Physik. Chem.," 57, p. 117, 1907.

[||] "Journ." Amer. Chem. Soc., 31, p. 353, 1909.

[¶] *Cf.* Nernst, Garrard and Oppermann, "Gött. Nachr.," 56, p. 86, 1900.

$$w\left\{\frac{1}{d}-\frac{a+c}{c}n\delta+\frac{uC-vA}{(u+v)c}g\gamma\right\}$$

if we suppose the volume changes to be unaffected by the presence of the non-electrolyte.

From this we get

$$\{(1-n)C-nA\}=\frac{c}{g\gamma}\left\{\frac{l''}{wr}-\frac{1}{d}+\frac{a+c}{c}n\delta\right\},$$

where l'' is the mass of non-electrolyte lost by the cathode vessel during the migration experiment. Hence, if l'' be measured, the hydration factor can be determined when $\left(\frac{1}{d}-\frac{a+c}{c}n\delta\right)$ is known sufficiently accurately, or is, as sometimes happens, small enough to be neglected.

For a solution containing 1·25 gm. mols. of Na Cl per litre, Washburn found by Hittorf's method $n_H=0{\cdot}634$, and from this, when the hydration factor was determined in the way indicated above, he obtained $n=v/(u+v)=0{\cdot}617$.

More could be said concerning the interest* which is attached to the determination of migration constants, for example their relation to diffusion constants† has been left untouched; but I venture to hope that these Notes,‡ rather hurriedly written, and perhaps not free from numerical errors, may be of some general interest and may encourage Mrs. Griffiths to continue her work.

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* *Cf.* Mrs. Griffiths, concluding paragraph, *l.c.*, p. 146.

† *Cf.*, *e.g.*, the diffusion data given by B. W. Clack, "Proc." Phys. Soc., 27, p. 63, 1914, with the corresponding migration data, Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 201, 1898.

‡ Which are a version of the contribution to the discussion on Mrs. Griffiths' Paper, referred to on p. 316.

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